The Carbonization of Aromatic Hydrocarbons

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I. Introduction

Carbonization is the thermal conversion of organic materials to carbon and graphite. The overall transformation involves a complex series of chemical reactions and diffusion processes in both the liquid and solid state. The reaction sequence consists of the elimination of substituent atoms and groups from the organic molecule, aromatization, and subsequent polymerization to a large aromatic carbon framework.

Any organic material can be converted to carbon. Commercially, synthetic carbon and graphite are prepared from aromatic starting materials such as coal tar pitch and heavy petroleum residues. These raw materials consist largely of mixtures of compounds containing aromatic hydrocarbon and hetero-cyclic structures. We have found that the carbonization behavior of complex raw materials can be understood on the basis of the thermal reactions of relatively few, representative aromatic hydrocarbons. This paper reviews previous work and also presents results of our recent studies of the carbonization of several pure aromatic hydrocarbons.

## II. Chemical Constitution of Pitch

The carbonization of an organic material proceeds through an initial aromatic stage. Coal tar pitch is an example of such an aromatic stage formed during the pyrolysis of coal. There have been numerous compilations of the chemical constituents of coal tar pitch. [1, 2] These compilations include several hundred aromatic hydrocarbon and heterocyclic compounds. Table I lists the major aromatic hydrocarbon components that have been quantitatively determined in a typical coal tar pitch. The 13 structures shown constitute 13.6 percent of the entire pitch. The remainder of the material is composed of small amounts of hundreds of other aromatic compounds.

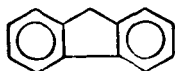## III. Thermal Reactivity and Aromatic Structure

The aromatic hydrocarbon components of pitch vary widely in thermal reactivity. This thermal reactivity is directly related to molecular structure. Table II compares the effect of chemical structure on the thermal reactivity of a number of hydrocarbons. The thermal reactivity is indicated by the lowest temperature at which an initial reaction is observed. Also listed are the corresponding ionization potentials derived from the optical absorption fre-quencies of the longest wavelength p-bands. [3] It is apparent that thermal reactivity increases with decreasing ionization potential. The presence of substituent groups on the aromatic ring can significantly alter these thermal reactivities either by providing a reaction site, or by altering the relative bond strengths in the molecule. [4]
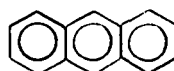
Table I

Some Aromatic Hydrocarbon Components of Coal Tar Pitch and their Occurrence in Weight Percent
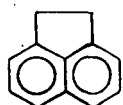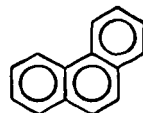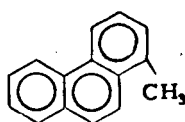
Acenaphthene
0. 3

Fluorene
0. 1

Anthracene + Phenanthrene
1. 2

Fluoranthene
1. 5
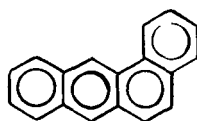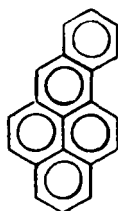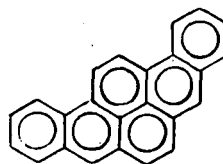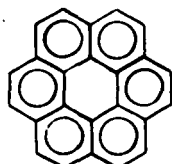
Pyrene
1. 3

Methylphenanthrene
0. 3
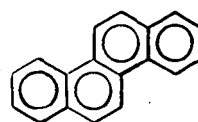
Chrysene
2. 7

Benz-(a)-anthracene
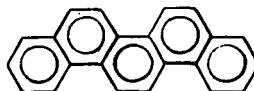0. 7

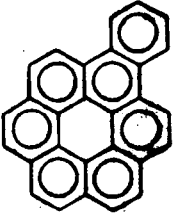Benzo-(a)-pyrene
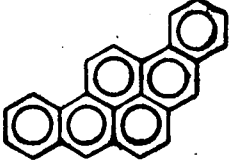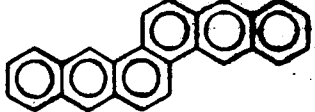3. 6

3, 4, 9, 10-Dibenzopyrene
1. 5

Coronene

Picene

Table II

Relation of Thermal Reactivity to Aromatic Structure

Aromatic Hydrocarbon	Reaction Temp. °C	Ionization Potential (eV)
	637	7.24
	560	7.07
	535	6.86
	480	6.64
	411	6.23

IV. Effects of Chemical Structure on the Nature of the Final Graphite

The heat treatment of organic materials to 3,000°C results in carbons possessing basically the graphite structure. The degree of graphitization and the properties of synthetic carbons obtained at 3,000°C are determined largely by the structure of the starting material. This effect is illustrated by the data in Tables III and IV which give the X-ray semilattice spacings for 3,000°C carbons prepared from a variety of aromatic hydrocarbons.

Table III includes well-graphitizing compounds which possess c-spacings between 3.354 and 3.363Å. Natural graphite has a c-spacing of 3.354Å. Table IV lists some poorly graphitizing materials. The high c-spacings, 3.370 to 3.44, obtained for these materials indicate a much more disordered carbon structure. It is not generally obvious from the initial chemical structures in Tables III and IV how well a given aromatic hydrocarbon will graphitize. For example, the 5-membered ring aromatic hydrocarbon acenaphthylene yields a well-ordered graphite, while the highly symmetrical molecule coronene gives rise to a poorly ordered graphite. However, sterically overcrowded and nonplanar molecules generally lead to more disordered graphite structures. [5]

V. Carbonization of Acenaphthylene and Terphenyl

The chemical transformations which occur during carbonization can be aptly demonstrated by the coking behavior of two representative aromatic hydrocarbons, acenaphthylene (I) and p-terphenyl (II). Acenaphthylene produces an extremely well-graphitizing carbon, while p-terphenyl yields a disordered, nongraphitizing carbon.
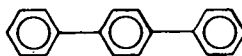
Acenaphthylene   p-Terphenyl
(I)   (II)

As with all organic materials, the carbonization of these hydrocarbons involves the removal of substituent hydrogen and the polymerization of the aromatic carbon residue. Three methods which we have found particularly useful for following these processes are: elementary analysis, X-ray, and diamagnetic susceptibility.

Figure 1 shows a plot of hydrogen content for acenaphthylene and p-terphenyl cokes versus heat-treatment temperature. The terphenyl does not react at all below 500°C. Between 500°C and 700°C the decrease in hydrogen content is more rapid for the terphenyl, while above 700°C the acenaphthylene dehydrogenation proceeds faster.

Figure 2 presents some X-ray data obtained by Ruland[6, 7] for the same series of samples. The growth of average aromatic layer size, L_a, is plotted versus temperature. The terphenyl shows an extremely rapid growth of L_a to 800°C, followed by a much slower growth rate at higher temperatures. For acenaphthylene, the polymerization of aromatic layers is much more gradual below 700°C but eventually surpasses the terphenyl. [7]

Table III

Effects of Aromatic Structure on the c-Spacings of 3,000°C Carbons
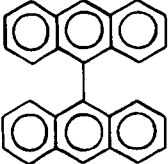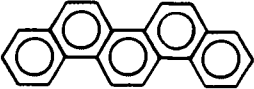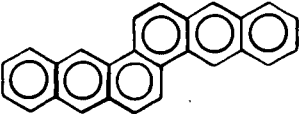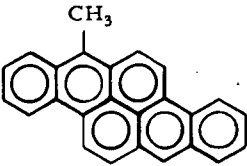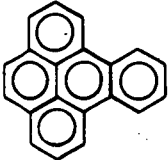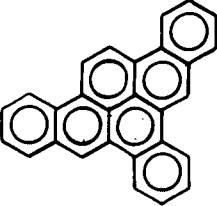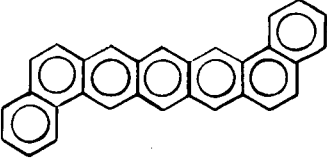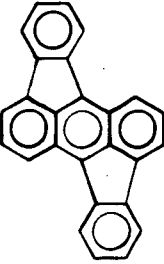
Structure	002, Å	Structure	002, Å
	3.354		3.357
	3.354		3.358
	3.356		3.358
	3.356		3.358
	3.356		3.363

Table IV

Effects of Aromatic Structure on the c-Spacings of 3,000°C Carbons
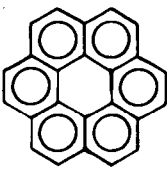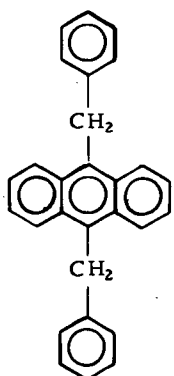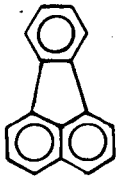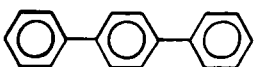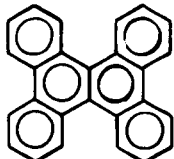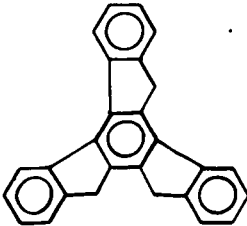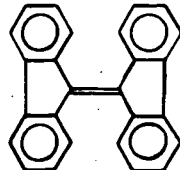
Structure	002, Å	Structure	002, Å
	3.370		3.41
	3.371		3.44
	3.373		
	3.385		3.44

Figure 3 contains a plot of magnetic susceptibility data obtained by Wagoner[8] for these two compounds heat treated to 3,000°C. The terphenyl shows a slight decrease in X between 500° and 700°C, and then an increase with temperature to a maximum at 3,000°C. The acenaphthylene shows a more pronounced dip in X between 500° and 800°C than observed for terphenyl. This decrease in susceptibility is presumably due to a paramagnetic contribution from free radicals. The acenaphthylene exhibits a lower diamagnetic susceptibility than terphenyl up to about 1,600°C, while above this temperature the aromatic layer growth is much more rapid for acenaphthylene.

All these data indicate that the aromatic polymerization process is much more rapid at low temperature for the more disordered terphenyl system. However, the initially-formed polymers from terphenyl are structurally not as suitable for continued aromatic growth to graphite as the much smaller polymers initially produced from acenaphthylene.

The dehydrogenation-polymerization process which leads to the formation of carbon is still poorly understood. This point is illustrated by the data plotted in Figure 4. From elementary analysis and X-ray data, the number of carbon and hydrogen atoms per fused aromatic molecule have been estimated and plotted as a function of temperature for both acenaphthylene and terphenyl cokes. Also included in Figure 4 is a theoretical plot of carbon versus hydrogen content for the most highly condensed aromatic hydrocarbon molecule. Up to about 600°C the acenaphthylene and terphenyl curves fall close to the theoretical line. The reactions occurring in this region appear to involve the removal of a hydrogen atom from the aromatic ring to form a simple free radical. At 700°C and above, multiple hydrogen atoms are eliminated leaving aromatic molecules with many unsubstituted edge sites. This process appears to proceed more readily for acenaphthylene than for terphenyl.

The nature of the bonding of the free electrons in these molecules is not clear. The interpretation of electron spin resonance measurements of materials in this region is complicated by the onset of electrical conductivity and magnetic anisotropy.[9]

VI. Chemical Reactions of Carbonization

We can delineate the kinds of chemical reactions which occur during the early stages of coking by studying the carbonization of several aromatic hydrocarbons. Their initial reactions lead to the intermediates which control the subsequent course of carbonization. There are three types of thermal reaction processes which are important. (1) dehydrogenation, (2) rearrangement, and (3) polymerization. These reactions do not proceed in distinct steps, but occur continuously throughout the coking process. Several examples of these reactions follow.

A. Dehydrogenation

The initial reaction in carbonization involves the loss of a hydrogen atom from an aromatic hydrocarbon and leads to the formation of an aromatic free radical intermediate. If the free radical intermediate is stable, it can then be detected by electron spin resonance. In the liquid state, usually all but the most stable free radicals will rearrange or polymerize. The phenalenyl radical (III) is an example of an extremely stable free radical produced by simple hydrogen dissociation reaction at room temperature.
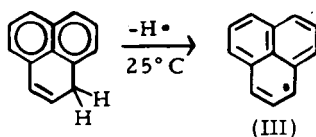
It can be well characterized by its simple ESR spectrum. [10]

The hydrocarbons fluoranthene and naphthalene polymerize directly with the direct loss of hydrogen. The unstable free radicals (IV) and (V) can be postulated as intermediates in these reactions.
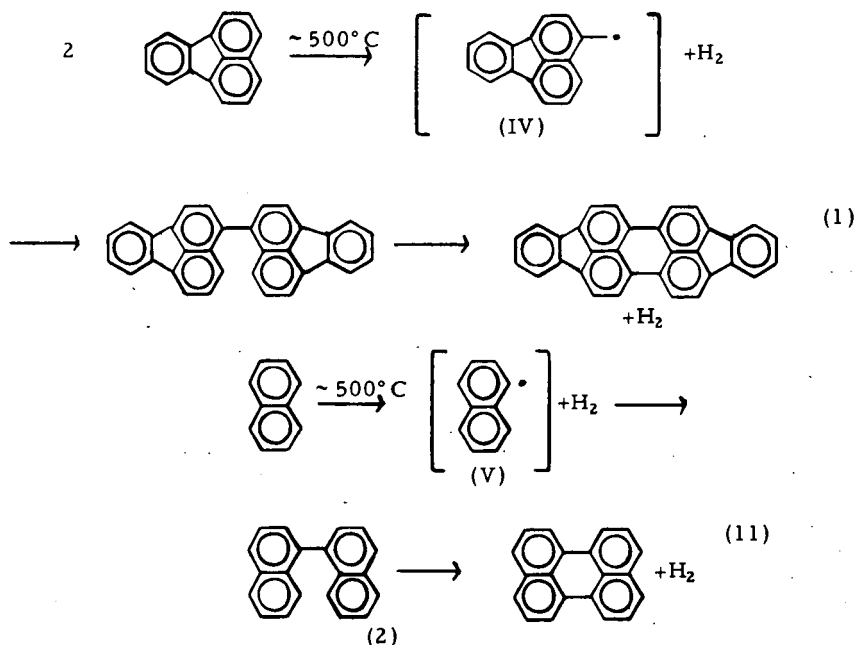
In many instances the dehydrogenation of aromatic hydrocarbons appears to involve bimolecular hydrogen transfer reactions. Hydrogenated aromatic hydrocarbons are often identified in the volatile products of carbonization. [4] These reactions usually occur at the most reactive site on the aromatic molecule. A typical hydrogen transfer sequence is illustrated for the hydrocarbon naphthacene:

Dihydronaphthacene
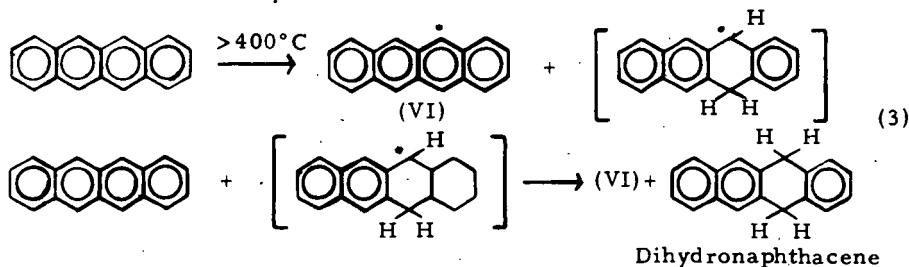
The volatile 5, 12-dihydronaphthacene is a major reaction product during the initial stages of reaction. It is not clear whether the intense but unresolved ESR signal observed during the onset of pyrolysis of naphthacene is due to the radical (VI). [12]

It should be pointed out that if there is a carbon-carbon single bond available, thermal cleavage will occur at this site. The thermally produced free radical can then participate in hydrogen transfer reactions. This reaction is illustrated in the pyrolysis of 9,9'-bifluorene (VII).

(VII)   (VIII)

fluorene $\Delta^{9, 9'}$-bifluorene
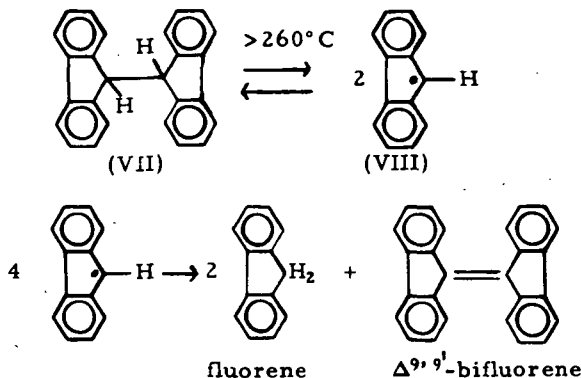
At about 260°C (VII) dissociates to produce the fluorenyl radical (VIII). This species has been detected by ESR. [12] At higher temperatures a hydrogen transfer reaction leads to fluorene and $\Delta^{9, 9'}$-bifluorene as the major products. The reactive phenyl radicals produced from the pyrolysis of terphenyl also undergo hydrogen transfer processes, since benzene and biphenyl are among the reaction products.

B. Rearrangement Reactions

Perhaps the most complicating features of the early stages of carbonization are the thermal rearrangements reactions. They often make it impossible to predict from the starting structure whether a given compound will produce a well-graphitizing or a disordered carbon. Thermal rearrangement usually leads to a more stabilized aromatic ring system which can then become the building block for graphite growth. Several examples of the thermal rearrangement of aromatic hydrocarbons follows.

1. Conversion of $\Delta^{9, 9'}$-bifluorene to tetrabenzonaphthalene.
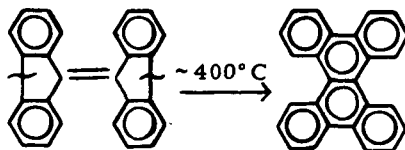
2. Conversion of biacenaphthylidene to zethrene.
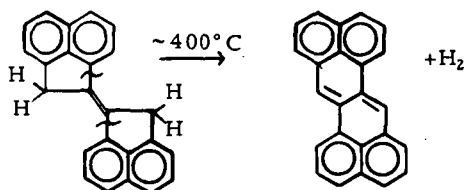
3. Formation of rubicene from $\Delta^{9,9'}$-bifluorene.
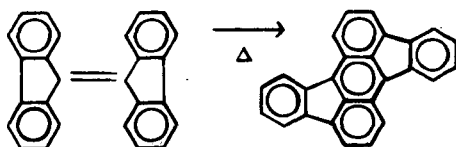
In some instances thermal rearrangement can involve a carbon-carbon bond cleavage within a condensed aromatic ring. These reactions are higher energy processes and are usually observed at very high temperatures, as in vapor phase pyrolysis.
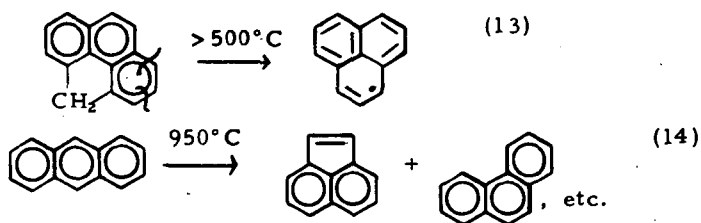
C. Polymerization of Aromatic Radicals

The formation of carbon involves the polymerization of aromatic free radicals. These polymerizations usually initiate in the liquid phase and lead to solid aromatic polymers. This step is an important stage in the graphitization process. [15]

Unlike conventional polymerization reactions which rapidly increase the molecular size, the aromatic polymerization appears to proceed in steps. [6] The following examples show the formation of dimers and trimers during the first stages of polymerization of aromatic radicals.

(1)

(2) (14) (16)

(3) (11) (17)

(4) (6)

(IX)
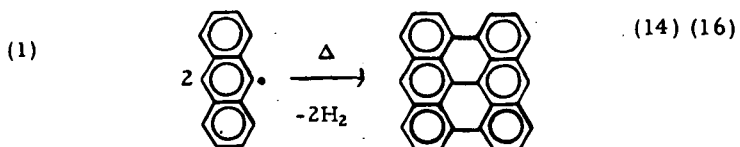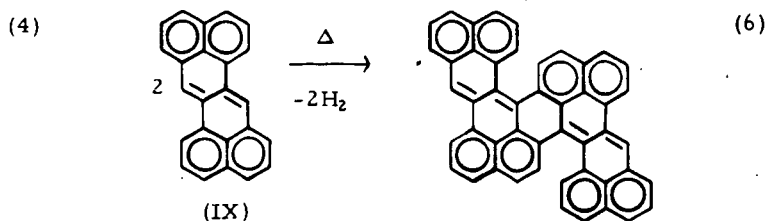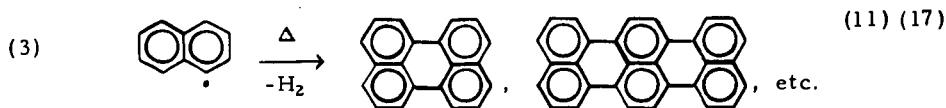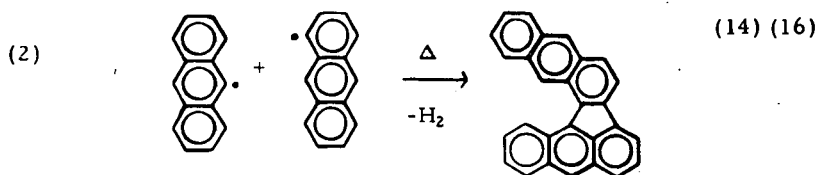
The most important criterion for obtaining a well-ordered graphite is to have the right "building blocks" from the standpoint of reactivity and steric configuration.[18] A molecule such as zethrene meets these requirements since it can polymerize at its most reactive positions and give rise to a condensed aromatic polymer without vacancies (see X). Nonplanar radical intermediates, such as those produced from $\Delta^{9,9'}$-bifluorene or p-terphenyl, lead to disordered aromatic polymers which never truly graphitize.
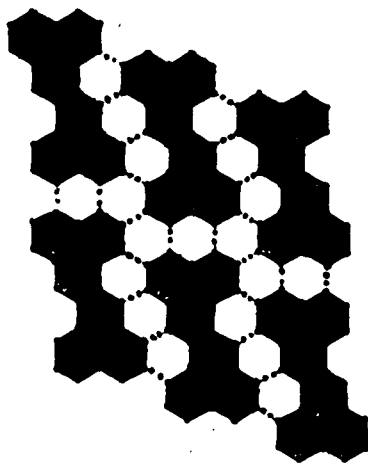
(X)

VII. Conclusions

The formation of synthetic carbon and graphite involves the thermal dehydrogenation and polymerization of aromatic hydrocarbons. The thermal reactivity and the course of carbonization are controlled by the structure of the starting aromatic molecule. More rapid reaction during the early stages of carbonization usually leads to a more disordered graphite structure.

Chemical studies on the pyrolysis of representative individual aromatic hydrocarbons show the importance of 3 types of thermal chemical reactions: (1) dehydrogenation, (2) rearrangement, and (3) polymerization. The nature of the final graphite and the course of carbonization appear to be related to the structure and reactivity of the aromatic free radical intermediates, which are the building blocks for subsequent carbonization and graphitization.
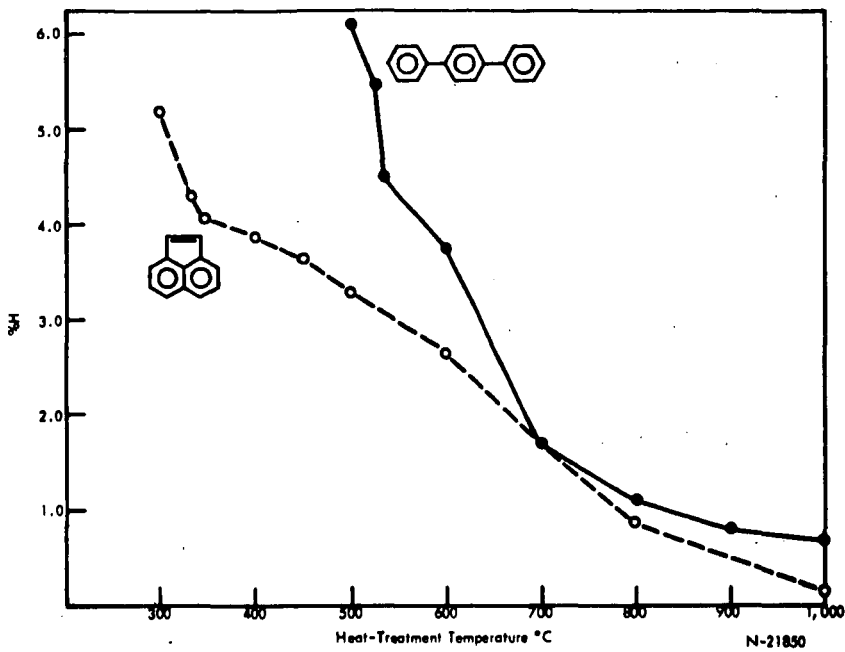
Figure 1. Elementary Analysis of the Products of Carbonization of Acenaphthylene
and p-Terphenyl; Weight Percent Hydrogen vs. Heat Treatment Temperature

N-21850
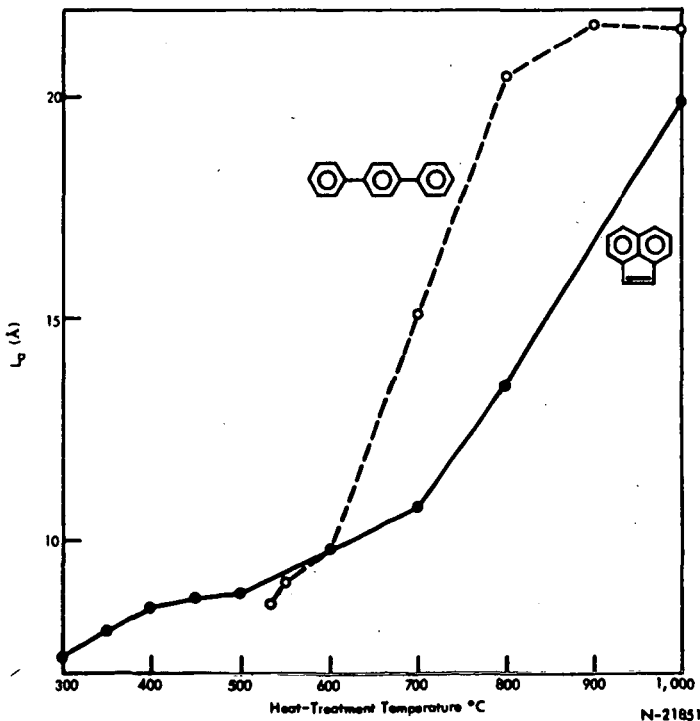
Figure 2. Aromatic Layer Growth in the Carbonization of Acenaphthylene and p-Terphenyl;
L_a (Å) vs. Heat-Treatment Temperature.

N-21851
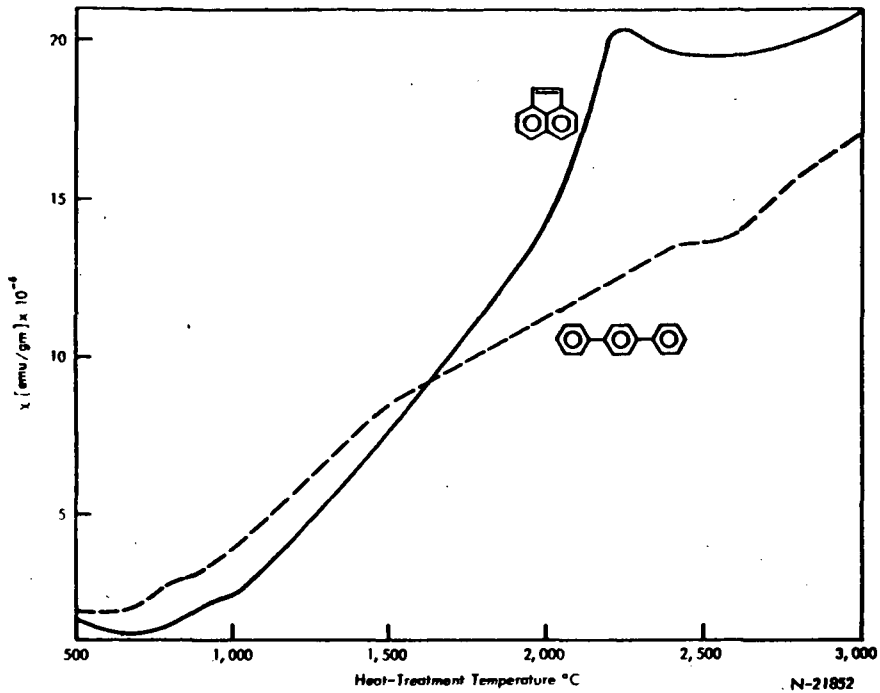
Figure 3. Static Magnetic Susceptibility of Acenaphthylene and p-Terphenyl
as a Function of Heat-Treatment Temperature
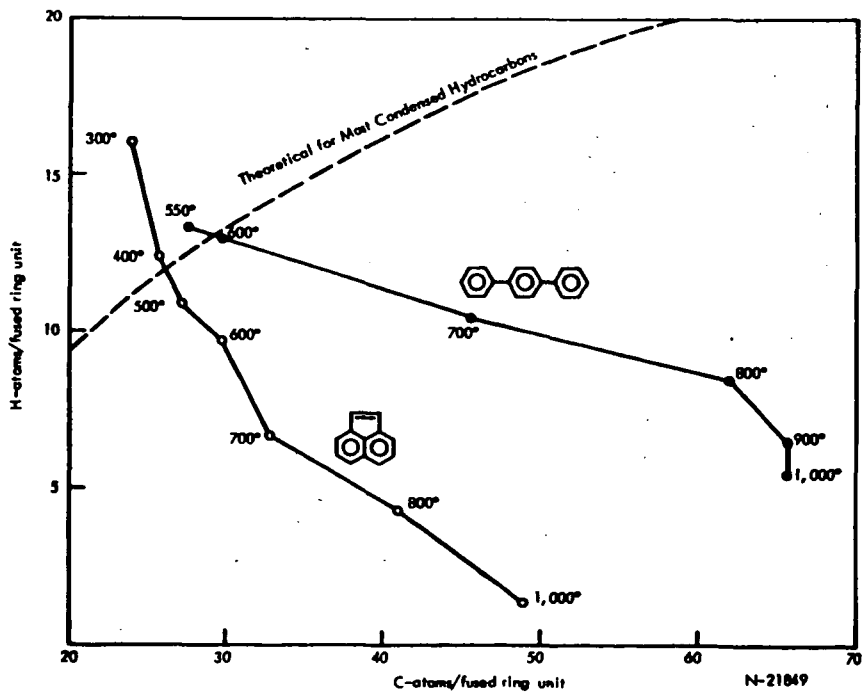
Figure 4. Dehydrogenation-Polymerization Diagram for Heat-Treated Acenaphthylene and p-Terphenyl

References

(1) "The Coal Tar Data Book," Coal Tar Research Association, Oxford Road, Gomersal, Nr. Leeds, Percyland, Humphries and Co. Ltd., London 1963.

(2) "Bituminous Materials: Asphalts, Tars, and Pitches," Vol. III, Interscience Publishers, New York, N.Y., (1966), pp. 139-216.

(3) F. A. Matsen, J. Chem. Phys., 24, 602 (1956).

(4) I. C. Lewis and T. Edstrom, J. Org. Chem., 28, 2050 (1963).

(5) T. Edstrom and I. C. Lewis, Carbon 7, 85 (1969).

(6) W. Ruland, Carbon 2, 365 (1965).

(7) W. Ruland, unpublished results.

(8) G. Wagoner, unpublished results.

(9) L. S. Singer and A. R. Cherry, Abstracts of the 9th Carbon Conference, Boston, (1969).

(10) For a review of ESR measurements of phenalenyl, cf., I. C. Lewis and L. S. Singer, J. Phys. Chem., 73, 215 (1969).

(11) K. F. Lang, H. Buffleb and J. Kalowy, Chem. Ber., 90, 2888 (1957).

(12) I. C. Lewis and L. S. Singer, Carbon 5, 373 (1967).

(13) L. S. Singer and I. C. Lewis, Carbon 2, 115 (1964).

(14) G. M. Badger, J. K. Donnelly, and T. M. Spotswood, Aust. J. Chem., 17, 1147 (1964).

(15) J. D. Brooks and G. H. Taylor, "Chemistry and Physics of Carbon," Volume 4, Marcel Dekker, Inc., New York, 1968, pp. 243-286.

(16) K. F. Lang, and H. Buffleb, Chem. Ber., 94, 1075 (1961).

(17) G. H. Badger, "Progress in Physical Organic Chemistry," Vol. 3, 1 (1965).

(18) I. C. Lewis and L. S. Singer, Carbon 7, 93 (1969).

STRUCTURAL CHANGES ACCOMPANYING
COKE CALCINATION

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INTRODUCTION

Although a voluminous number of articles have been published on the structural changes occurring in carbons upon heat treatment over a wide 1200°C-2800°C temperature range, similar information for the narrow 500°C-1200°C calcination range is rather sparse. A few articles[1-4] have been written in which properties such as density, electrical resistivity and pore structure have been correlated with temperature of calcination and time at maximum temperature. It is, however, difficult to relate the various experimental results and conclusions reported. In this study the progression of structural changes occurring during the calcination of four raw coke samples from different sources was followed using high temperature microscopy techniques. Concurrent with the examination of the topographical features, the transformation of the microstructure of the carbons was studied by means of x-ray diffraction and mercury porosimetry.

EXPERIMENTAL

The high temperature microscopic examinations were performed using a Leitz Ortholux microscope equipped with a Leitz vacuum heating stage. Thin polished sections (∿0.03" thick) of the cokes were placed on a hollow graphite cylinder encompassing a Pt + 10% Rh vs. Pt thermocouple which had been calibrated against the melting points of several pure compounds. The sample and sample holder were then radiantly heated at a rate of ca. 30°C/minute in an inert atmosphere. A holding time of 5-10 minutes was allowed at each temperature to establish thermal equilibrium. Two representative areas were selected from each sample and photographed at a magnification of 35X with parallel and crossed nicols in the raw state, 300°C and at increments of 100°C to 1000°C. The dimensional and structural changes were obtained from 100X photographic enlargements.

In a complementary microscopic study relatively large lumps of the raw cokes were polished, and suitable areas were selected and photographed at 10X. These samples were then successively heated from 500°C to 1200°C in 100°C increments at a rate of 5°C/minute.

A 15,000 psi Aminco mercury porosimeter was used to obtain micropore volume distribution in representative samples of each coke as a function of heat treatment. The samples were crushed to 10/20 mesh particle size and duplicate measurements made on 0.5 g. samples.

X-ray diffraction studies were carried out employing a recording diffractometer using monochromatic Cu Kα radiation. Crystallite size values were obtained using the Scherrer formula with KCl as an internal standard.

RESULTS

A total of four cokes was studied in this investigation. As
indicated by the characteristics of the four cokes listed in Table
I, these samples are representative of an anisotropic coke (sample
A&B) and an isotropic coke (sample C&D). The ash and sulfur contents
and real densities of the raw cokes represent the range of values
generally encountered with commercial cokes.

The type of changes in topographical features which the cokes
underwent during calcination as revealed under the hot stage micro-
scope are illustrated in Figure 1. The structure of the raw coke
could be determined only with the aid of polarized light. Heating
to 700°C produced very little change in the appearance of the
polished surface of the samples except, perhaps, a slight increase
in the width of existing cracks. Suddenly at 800°C, the detailed
structure of the coke could be observed under parallel nicols.
Further increase in temperature resulted in progressive opening
of existing cracks, apparent creation of a few small cracks, and
an obvious overall shrinkage. However, the basic macrostructure
of the calcined coke was essentially the same as observed in the
raw coke under polarized light. The two isotropic cokes had areas
of pitch and mesophase which melted upon heating above 500°C
producing voids lined with highly anisotropic carbon.

The magnitude of the dimensional changes observed as a function
of temperature are illustrated in Figure 2 representing results typ-
ical of an anisotropic coke and in Figure 3 for a coke with an
isotropic structure. The curves were plotted from data obtained
with the hot stage (micro) and from ambient temperature measure-
ments on the coke lump samples (macro). Considering the high
temperature microscopy experiments, it should be noted that the
dimensional changes recorded include the reversible thermal expansion
of the carbon as well as shrinkage. The 1.0% to 2.5% linear
expansion observed in all of the coke samples upon heating to 500°C
is a manifestation of the reversible expansion. Contraction of the
coke begins after 500°C with the maximum rate of dimensional change
occurring between 700°C and 800°C. It is also significant to note
in this same temperature range the marked shrinkage in the direction
perpendicular to the needle structure as compared to that occurring
parallel to the needle structure for the anisotropic cokes.

The information derived from the larger samples at room tempera-
ture correlates well with the high temperature measurements. The
two sets of curves are similar in shape and the cross-over point
of the shrinkage perpendicular and parallel to the flow structure
occurs, within experimental error, at the same temperature. The
weight losses calculated from these experiments suggest, as one
would expect, a general direct relationship with the volatile content.
Of more interest is the change in slope observed in the curves repre-
senting weight loss as a function of temperature which occurs in the
700°C to 800°C temperature range. This information for the two
anisotropic and two isotropic cokes is given in Figure 4.

Mercury porosimetry measurements of 10/20M fractions were used
to determine the accessible pore volume at each of the heat treatment
temperatures. Pore volumes were determined in two pore size ranges,
V_2 for pore diameters between 65 and 12μ and V_1 for diameters between
12 and 0.015μ. Although a gradual increase in V_2 with increasing

temperature was noted for all of the cokes, the results were usually
erratic and appeared to reflect gross, non-uniform structural changes.
The V_1 porosity behavior, as illustrated in Figure 5, is generally
the same for both types of cokes. There is an overall increase in
accessible porosity with increasing temperature. This increase in
porosity is considered to be due to the formation of shrinkage cracks
resulting primarily from loss of volatiles during calcination. As
shown in Figure 5, three of the four cokes exhibited a relatively
abrupt increase in porosity beginning at about 900°C, which would
appear to be indicative of a significant structural change.

Changes in apparent density measured by mercury displacement
were also determined concurrent with the porosity measurements.
Figure 6 displays the trends in density change vs. temperature for
the two types of coke studied. The A. D.'s of the cokes were observed
to remain constant until 700°C-800°C at which point a sudden increase
in density occurred. These results correlate well with the hot stage
microscopy measurements where a significant linear shrinkage of the
samples was observed to occur in this temperature range.

The (002) x-ray diffraction peak intensities were measured on
the four cokes and plotted as a function of temperature. The peak
intensity measurements reflect the progressive ordering of the gra-
phitic planes during calcination. Figure 7 illustrates the extreme
cases of the anisotropic cokes compared with the isotropic cokes.
In all cases the peak intensity appears to increase at a logarithmic
rate with temperature; however the anisotropic cokes maintain peak
intensities of a higher magnitude throughout the calcination range
than the isotropic cokes.

The d-spacing, which is classically a measure of the graphitic
nature of carbon, was obtained for all samples as a function of tem-
perature. As might be expected, d-spacings were found to decrease
with increasing temperature. This is illustrated in Figure 8, where
it is of interest to note that while the isotropic cokes have large
d-spacings at the outset, the d-spacings of the anisotropic and
isotropic cokes are essentially equivalent by 1100°C. The low initial
d-spacings of the isotropic cokes are believed to be due to the
amorphous material contributing mainly to the background of the
diffraction curve. Only the highly graphitic portions of the sample
are detectable, which result in low d-spacing values not truly
representative of the entire sample. On the other hand, less amorphous
material is present in the anisotropic cokes, and a broader spectrum
of crystallite perfection is detectable. Therefore, the total value
of the d-spacings appears large. Other experiments conducted beyond
the 1200°C range have shown that the d-spacings of isotropic cokes
maintain higher values than the anisotropic cokes, which is in
agreement with the cross-over point at 1100°C in Figure 8.

The change in crystallite size along the c crystallographic axis
as a function of temperature was very similar for all cokes. This
relationship, presented in Figure 9 for the four cokes, is charac-
terized by a significant decrease in size between 500°C and 900°C;
after which a steady increase is observed up to 1200°C. Since the
Lc values represent an average of all detectable crystallites for a
given sample, it is believed that the initial decrease in Lc is due
to the appearance of a large number of extremely small crystallites
which have grown to a detectable size. This pronounced decrease in

Lc values at 600°C-700°C corresponds with the onset of the rapid shrinkage of the coke samples. It seems reasonable, therefore, to presume that the coke structure shrinkage is in part a result of its conversion to a more compact crystalline structure.

CONCLUSIONS

With only minor exceptions, the general overall structure of the calcined coke is predetermined in the raw state. With respect to microstructure, the dominant recurring theme running through our experimental data is the sudden changes which occur in the 600°C to 900°C temperature range. The sharp observed increase in dimensional shrinkage results from the loss of volatile constituents as well as ordering and growth of the polycrystalline structure. The increased microporosity represents the creation of shrinkage cracks as well as pores formed due to the escape of volatile components.

REFERENCES

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REFERENCES

1. P. L. Walker, Jr., F. Rusinko, Jr., J. F. Rakszawski, and L. M. Liggett. Proceedings of the Third Conference on Carbon, University of Buffalo (1957) p. 643.

2. C. F. Stout, M. Janes, and J. A. Biehl: WADD Technical Report 61-72, Vol. 36 (1964).

3. E. Barrillon, Carbon, 5, 167-171 (1967).

4. P. Rhedey, Transactions of the Metallurgical Society of AIME, 239 1084 (1967).

TABLE I

CHARACTERIZATION OF THE RAW COKES

Sample	Volatile Matter (%)	Ash (%)	Sulfur (%)	Real Density (g/cc)	002 Peak Intensity (c/s)	d-Spacing (Å)	X'tal Size Lc (Å)
Coke A	5.90	0.110	0.72	1.437	115	3.5131	25.6
Coke B	6.43	0.085	0.70	1.397	178	3.7745	23.6
Coke C	15.71	0.086	1.32	1.345	111	3.5186	30.1
Coke D	21.46	0.281	1.28	1.314	117	3.5118	32.6

FIGURE 1
STRUCTURAL CHANGES ACCOMPANYING
COKE CALCINATION
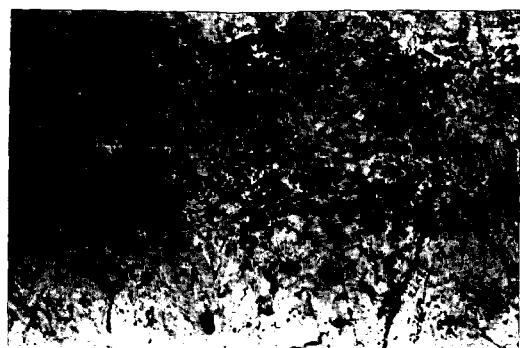
RAW (PARALLEL NICOLS)
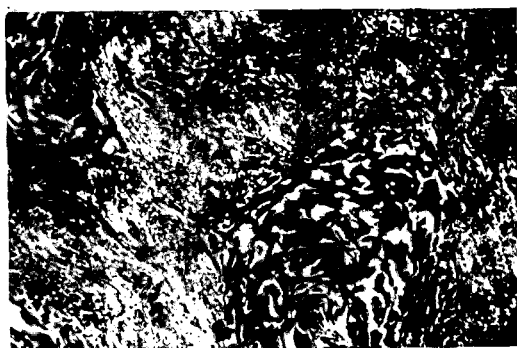
RAW (CROSSED NICOLS)
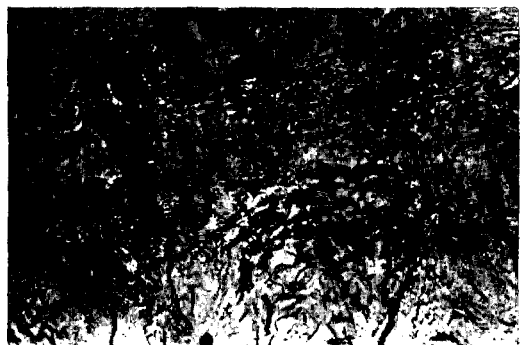
700°C (PARALLEL NICOLS)

800°C (PARALLEL NICOLS)

1000°C (PARALLEL NICOLS)

1000°C (CROSSED NICOLS)

100 μ

FIGURE 2
DIMENSIONAL CHANGES OF AN ANISOTROPIC COKE
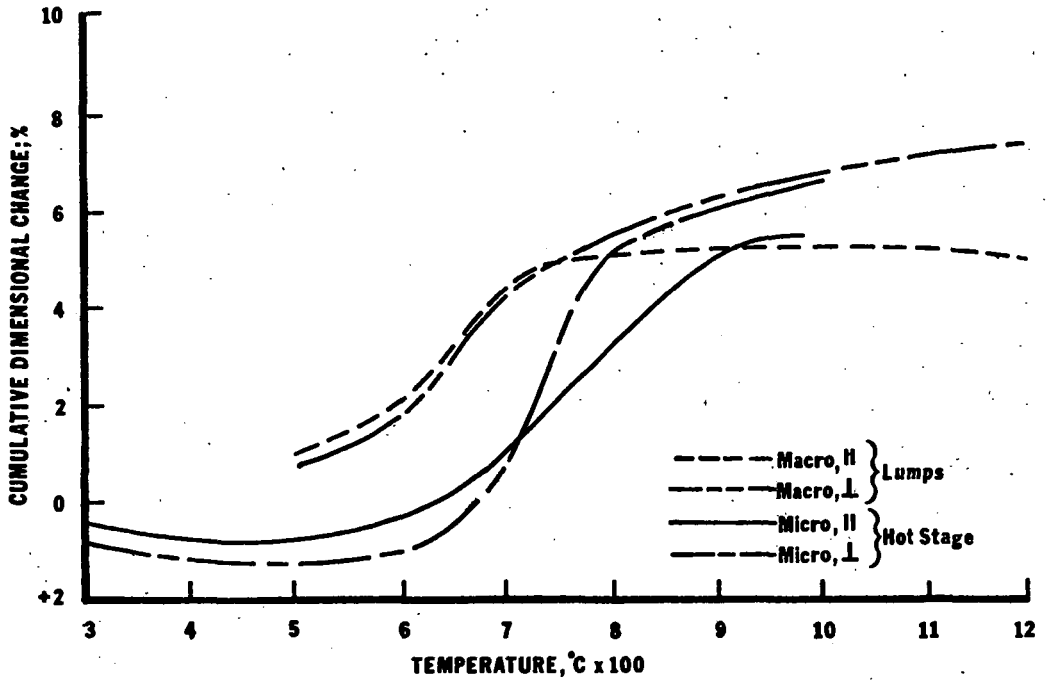
FIGURE 3
DIMENSIONAL CHANGES OF AN ISOTROPIC COKE

FIGURE 4
WEIGHT LOSSES vs TEMPERATURE

FIGURE 4
WEIGHT LOSSES vs TEMPERATURE

(y-axis: CUMULATIVE WEIGHT LOSS, %; x-axis: TEMPERATURE, °C x 100; curves labeled Isotropic Cokes and Anisotropic Cokes)
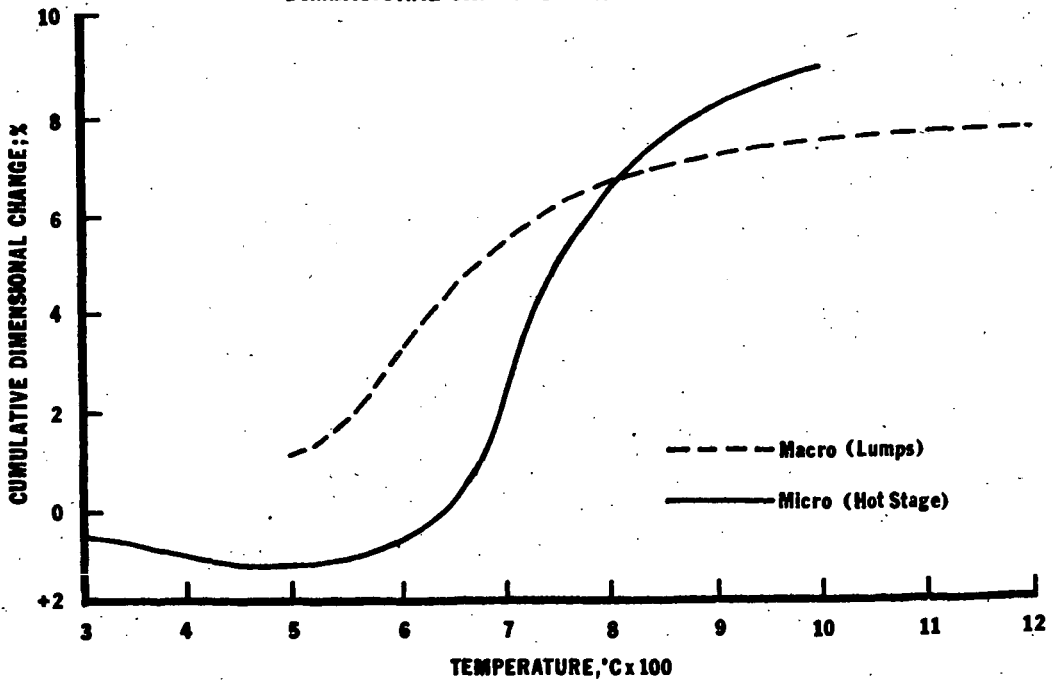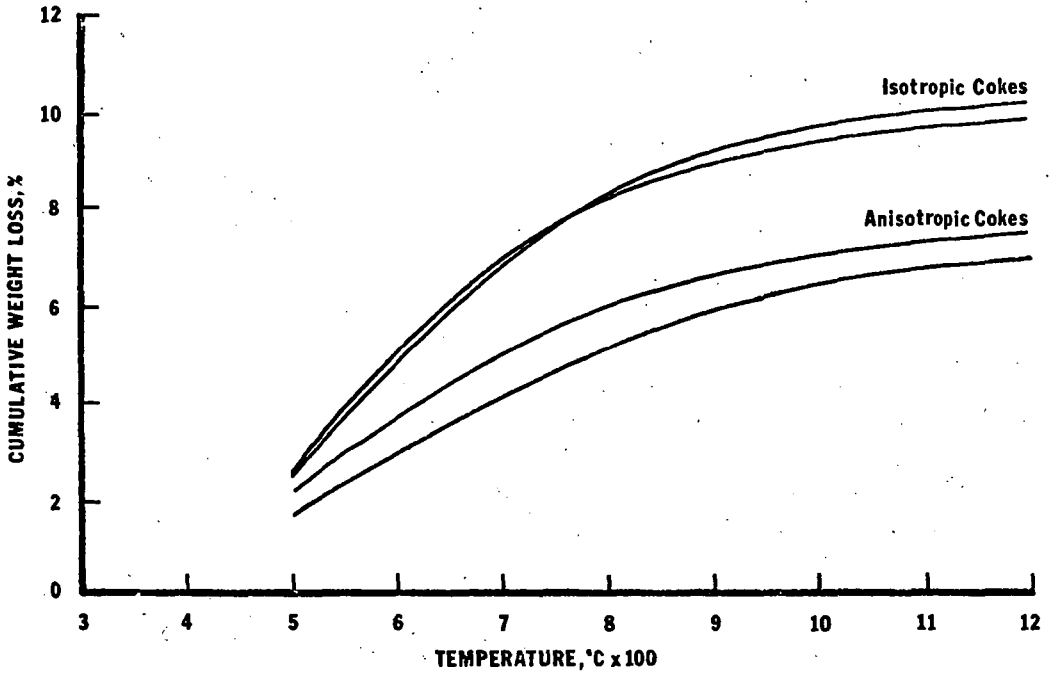
FIGURE 5
POROSITY vs TEMPERATURE OF VARIOUS COKES

FIGURE 5
POROSITY vs TEMPERATURE OF VARIOUS COKES

(y-axis: POROSITY (12−0.015a), mm³/gm; x-axis: TEMPERATURE, °C x 100; curves labeled Coke D, Coke C, Coke B, Coke A)

FIGURE 6
DENSITY vs TEMPERATURE

FIGURE 6
DENSITY vs TEMPERATURE

FIGURE 7
PEAK INTENSITY vs TEMPERATURE

FIGURE 7
PEAK INTENSITY vs TEMPERATURE

FIGURE 8
D-SPACING vs TEMPERATURE

FIGURE 8
D-SPACING vs TEMPERATURE

Anisotropic Cokes

Isotropic Cokes

D-SPACING (002), Å
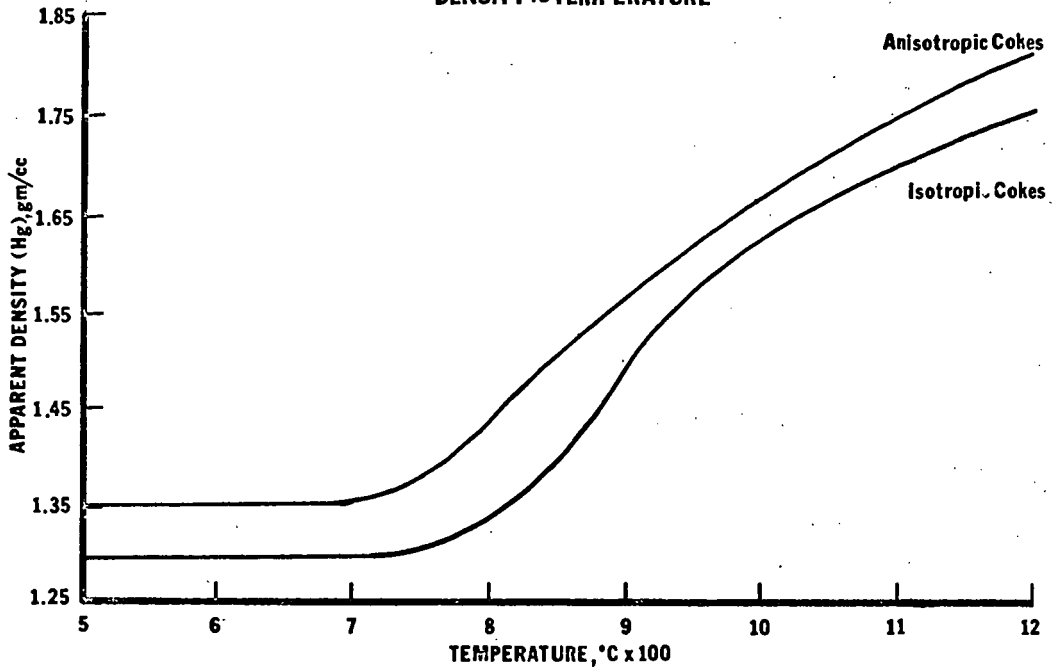
TEMPERATURE, °C x 100
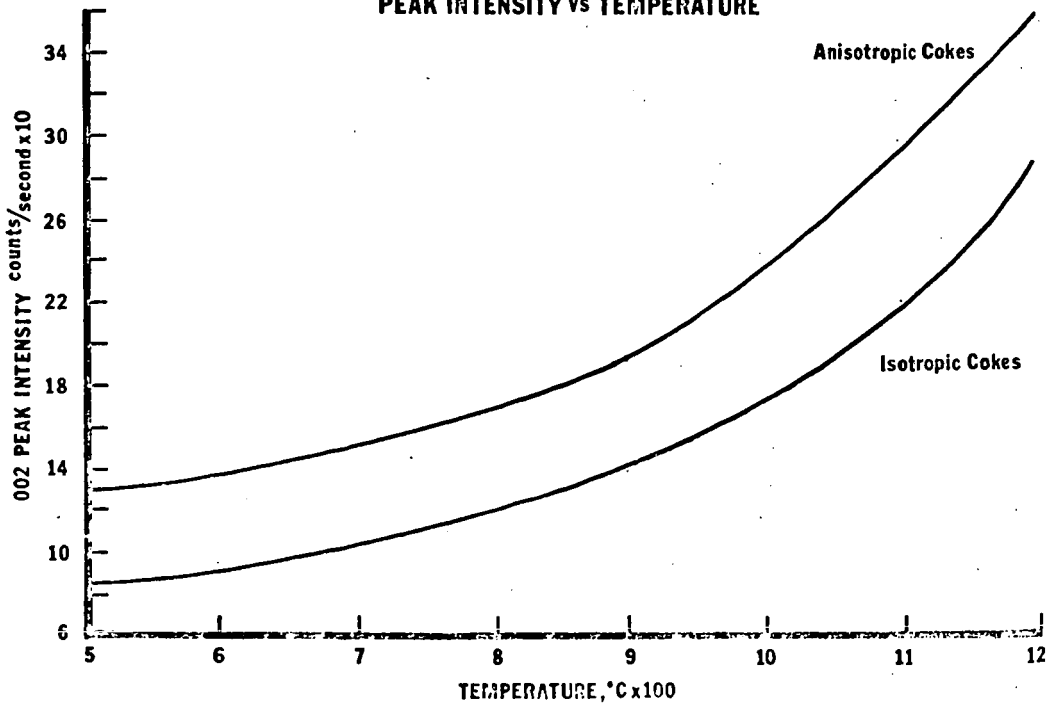
FIGURE 9
L$_C$ CRYSTALLITE SIZE vs TEMPERATURE

FIGURE 9
L$_C$ CRYSTALLITE SIZE vs TEMPERATURE

Isotropic Cokes

Anisotropic Cokes
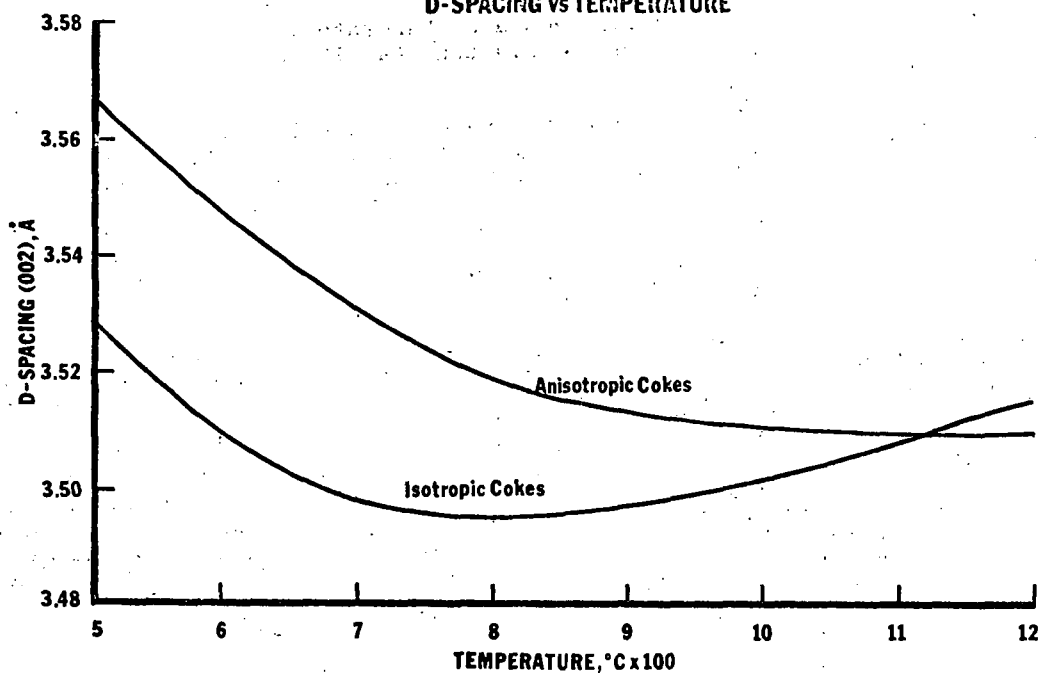
L$_C$ CRYSTALLITE SIZE, Å

TEMPERATURE, °C x 100
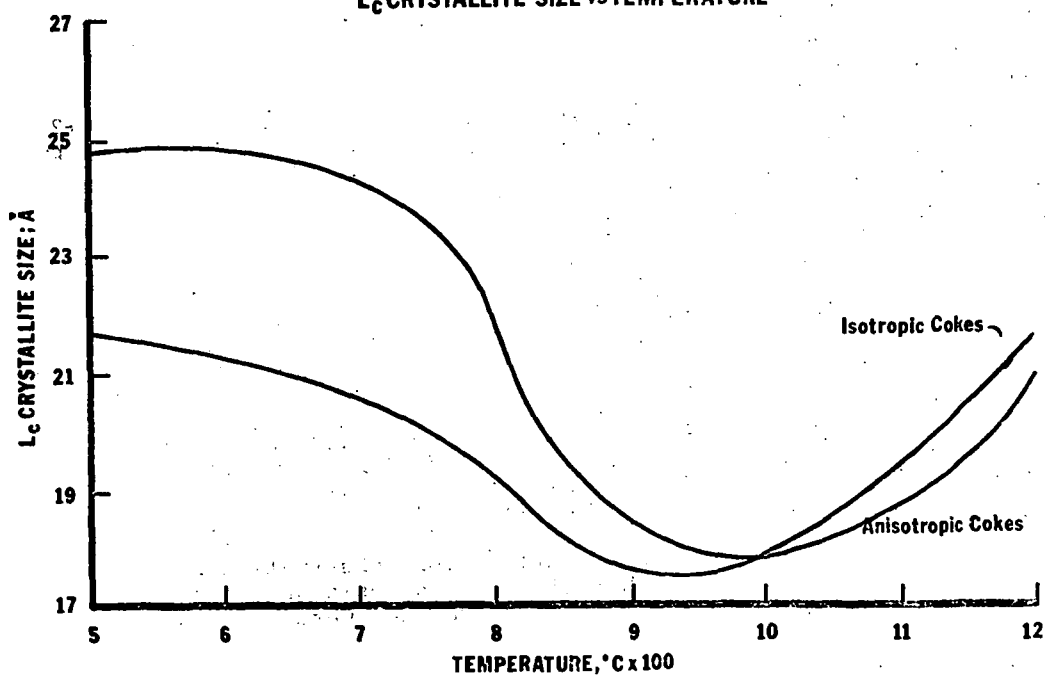
WETTABILITY OF PETROLEUM COKES BY PITCH

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In 1968 well over a million tons of petroleum coke were used in the United States in manufacturing carbon and graphite. For carbon anodes in aluminum smelting, delayed petroleum coke mixed with coke-oven pitch and subsequently baked has been used almost exclusively. While many investigations have been made on the properties required in binder pitches for carbon electrodes (1), there are no data on the characteristics of cokes other than impurity content and real density that relate to anode properties.

Microstructures of a variety of cokes and carbons were reported by Martin and Shea (2). In a petroleum coke, Kusakin et al, 1965 (3), observed two different types of particles: "spherulitic" particles, which are isotropic and relatively non-graphitizing, and a "streak" type, which is softer and graphitizing. Abramski and Mackowsky have developed methods for measuring in the microscope characteristic parameters for coke pores and walls (4). Other coke properties such as microporosity, macroporosity, and surface area have been measured. Rhedey (5) obtained a correlation between aggregate porosity and binder requirement of Soderberg paste for constant flowability. However, in none of the work is a correlation shown with baked anode properties.

A measurement related to porosity but more useful in assessing the effect of widely different calcined cokes on Soderberg anodes is the "wettability" by pitch. For the investigation reported here, an empirical procedure for measuring wettability was adapted from the elongation test used by Bowitz et al (6).

Procedure

In the modified elongation test, a mixture of 100 g -140 +200 mesh (Tyler) calcined coke and 120 g standard pitch (softening point 110°C, cube-in-air) was stirred in a small can at 160°C for 20 minutes with a spatula. Cylindrical specimens 45-50 mm long and 9 mm diameter were molded and cooled. The specimens were placed on the inclined board in an oven at 160°C for one hour. After cooling, the change in length (elongation) of the specimen was measured and the percent elongation calculated. The less an aggregate was wet by the standard pitch used in these tests, the greater was the elongation. The increased elongation was caused by the greater amount of pitch available in the space between coke particles because of decreased absorption into the pores.

Real densities were determined using a pycnometer with kerosene as the confining fluid (Alcoa Analytical Procedure 424). Microporosity was calculated as 100 times the difference between real density and the density with mercury as the confining fluid divided by the real density.

Samples were mounted for microscopic observation by impregnating at 29 in. Hg vacuum with Maraglas Type A resin and Maraglas hardener 555 (7). After standing overnight, samples were cured at 70°C for 16

hours. They were ground successively on 320, 2/0 and 4/0 grit papers
on a glass plate, polished on a wheel with Metaui 6 mu (Buhler, Ltd.),
with alpha alumina, and finally with gamma alumina.

For preparing baked anodes, an aggregate particle size distribu-
tion was used having the greatest dry bulk density as determined in a
series of settling experiments on a vibrating table. Cokes G and W
were used as 46.5 percent of the total aggregate in the coarse fraction
without crushing. The sizing of coke P was then adjusted for maximum
dry bulk density of the blend. Similarly, coke A was used in the fines,
as received, and the sizing of coke P was adjusted for maximum dry bulk
density. Anodes were made with about 27 percent pitch (softening point
105°C cube-in-air). The amount of pitch was adjusted so that all mixes
had the same elongation as determined on a specimen 2-1/2 in. long x
1 in. diameter molded from the green paste. Anodes 3 in. diameter x
4 in. tall were baked to 1000°C under 3.7 psi pressure. Baked apparent
density (BAD) and electrical resistivity were determined on the baked
samples.

Results

The elongation test procedure of Bowitz et al (6) specified 80
percent coke passing through a 200 mesh sieve. Lack of a lower limit
permitted a wide range in particle size and surface area of the sample.
In addition, the fine grinding could destroy much of the pore volume.
Preliminary tests demonstrated greater reproducibility when using five
fractions between 100 and 325 mesh (Tyler). The sizing finally chosen,
-140 +200 mesh, gave even better reproducibility. To increase ability
of the test to discriminate among cokes, the pitch content was in-
creased to 54.5 percent. Typical results are shown in Table 1 for two
successive mixes of coke P, with 18 specimens molded from each mix and
tested in the oven, six at a time.

Table 1

Reproducibility of Elongation Test for Coke P

	Elongation, %					
	Mix 1			Mix 2		
Test	1	2	3	1	2	3
	60.0	56.0	63.8	64.2	61.5	56.7
	58.1	57.6	63.2	64.0	64.3	59.3
	56.9	55.4	63.2	66.1	61.8	60.1
	53.4	54.0	60.1	61.9	59.5	62.2
	53.8	61.2	–	68.3	64.5	58.7
	61.2	58.7	–	63.7	65.8	64.7
Average	57.2	57.2	62.6	64.7	62.9	60.3
Std. deviation	3.99	2.58	1.66	2.21	2.35	2.34
Average for Mix 1	58.5%					
Average for Mix 2	62.6%					

For the particle size chosen, -140 +200 mesh, the accessible
porosity appeared completely filled with pitch because increasing mix-
ing temperature to 200°C and 230°C did not change the amount of
elongation. However, the degree to which pores in larger particles
were penetrated by pitch was affected by mixing temperature. For ex-
ample, with a typical anode aggregate (-4 mesh +pan) molded into 1-in.

diameter 2-in. long cylinders there was a marked decrease in elongation
with increased mixing temperature (Figure 1). At the lower mixing
temperature, viscosity of the pitch prevented substantial penetration
into the remote pores of the larger particles.

Three calcined delayed cokes had elongations from 61 to 227 per-
cent (Table 2), and the calcined fluid coke had an elongation of 355
percent. Anode properties, as measured by baked density and resistiv-
ity, varied with elongation and seemed to optimize at the intermediate
values of 186 and 227 percent. Anode properties did not correlate with
real density or the microporosity measurement of the calcined cokes.

Table 2

Properties of Calcined Cokes and Laboratory Anodes
Made from Mixtures with Coke P in the Aggregate

Coke	P	G	W	F
Process	Delayed	Delayed	Delayed	Fluid
Real Density	2.02	1.96	2.03	1.98
Microporosity	10.9	8.2	13.3	3.5
Elongation, %	61	186	227	355
Anode Properties				
Amount of Coke P in Aggregate	100	53.5	53.5	57.5
Baked app. density	1.39	1.44	1.43	1.41
ρ, ohm-in.	.0028	.0025	.0025	.0032

Microscopic examination showed that green delayed petroleum coke
(Figure 2) had the incipient pore structure of calcined coke (Figure 3).
In green coke the pores were filled, probably with a hardened residuum
from the coker feed, which distilled off during calcination and ex-
posed the pores and typical lamellar structure of calcined coke.

Although cokes P, G, and W were made by the delayed coking process,
each had a distinctive microstructure. Coke P (Figure 3) had the
lamellar and pore structure typical of many delayed cokes. Coke W
(Figure 4) had in addition a characteristic mottled structure. Coke G
(Figure 5) consisted of fused spherules, each having an onion-like
structure. Each spherule had a microporous surface coating.

The fluid Coke F (Figure 6) consisted of spherical particles, each
in turn frequently being made up of clusters of small spherules of
isotropic coke. Some of the larger particles had the onion-like
structure.

Discussion

The wide range of microstructures indicates the difficulty in
trying to find a single characterization factor for cokes in carbon
anodes. The wettability test, however, largely overcomes this ob-
jection since it is a direct measure of how the pore structure affects
the relationship between coke and binder. For example, the fluid coke

F, with its limited amount of surface accessible pores had poor wett-
ability as judged by elongation. Because of the poor bond between
coke and binder, fluid coke produced anodes with high resistivity.
This poor bond in anodes was clearly discernible in the microscope
(Figure 7). Attempts were made to alter the surface of Coke F to im-
prove the bond with binder pitch. Neither crushing to expose fresh
surface nor chemical etching with oxygen was successful (Table 3).

Table 3

Effect of Treatment of Coke F on Properties of Anodes Containing 20% of Coke F

Treatment	Baked App. Density	Resistivity ohm-in.
Untreated	1.41	.0029
Crushed to -100 mesh	1.40	.0030
Oxidized at 1050° to 6% wt loss	1.38	.0031

This was consistent with the explanation that pores in the aggregate
accessible to the binder are necessary to produce a good bond. After
coking of the binder, the binder coke and aggregate coke are kept from
separating by the mechanical action of binder coke formed within the
pore system of the aggregate. Coke G formed an excellent bond with
the binder coke (Figure 8), probably because the binder was able to
penetrate the porous layer characteristically on the surface of this
coke (Figure 4).

Because coke P had a high wettability by binder, the green mix
required a high pitch content, and this may have been a factor in the
high resistivity. The large pores and laminations in Coke P may also
have contributed to the high resistivity by presenting a tortuous path
for current flow.

The cause of differences in microstructure of the delayed cokes is
not known. Since all were made by the same process, operating
variables such as recycle ratio could be a factor. The presence of
nuclei seems to favor isotropic coke. For example, needle coke, a non-
isotropic coke is made by a 2-step process in which the nuclei present
in the feed stock are first removed and the needle coke is prepared
from the clarified feed (8). Even more important for Coke G may be the
chemical nature of the feed to the delayed coker. It has been re-
ported (9,10) that heterocyclic structures tend to produce isotropic
cokes and the feed for Coke G had a relatively high nitrogen content.

For carbon manufacture the wettability test can be used to predict
behavior in anodes of cokes having a wide variety of microstructures.
Low wettability indicates a poor bond may be expected between baked
binder and coke, and this will cause high electrical resistivity. On
the other extreme, high wettability may indicate an extremely porous
coke whose interior pores unfilled with binder can cause high electrical
resistivity.

References

1. Weiler, J.F., "Chemistry of Coal Utilization" H.H. Lowry ed,
   John Wiley & sons, Inc., New York; Supplementary Vol. p 627 (1963)

2. Martin, S.W. and Shea, F.L. Jr., Ind. Eng. Chem. 50, 41 (1953)

3. Kusakin, K.P., Vyatkin, S.E. and Averina, M.V., Tsvetnye Metally 38, 65 (No. 10, 1965)

4. Abramski, C. and Mackowsky, Marie-Therese in "Handbuch der Mikro-skopie in der Technik, " Hugo Freund, ed, Umschah Verlag, Frankfort am Main (1959) 2, Part 1, p 311

5. Rhedey, P., Trans AIME 239, 1084 (1967)

6. Bowitz, D., Eftestol, T. and Selvik, R.A., "Extractive Metallurgy of Aluminum," Gary Gerard, ed. Interscience Publishers, New York (1963) 2, p 331

7. The Marblette Corporation, Long Island City, New York

8. Shea, F.L., U.S. Patent 2,775,549 - December 25, 1956

9. Blayden, H.E., Gibson, J., and Riley, H.L., J. Inst. Fuel, Wartime bulletin, pp 117-129 (1945)

10. Hutcheson, J.M. and Jenkins, M.L., "Second Conference on Industrial Carbon and Graphite," The Society of Chemical Industry (1966) p. 433
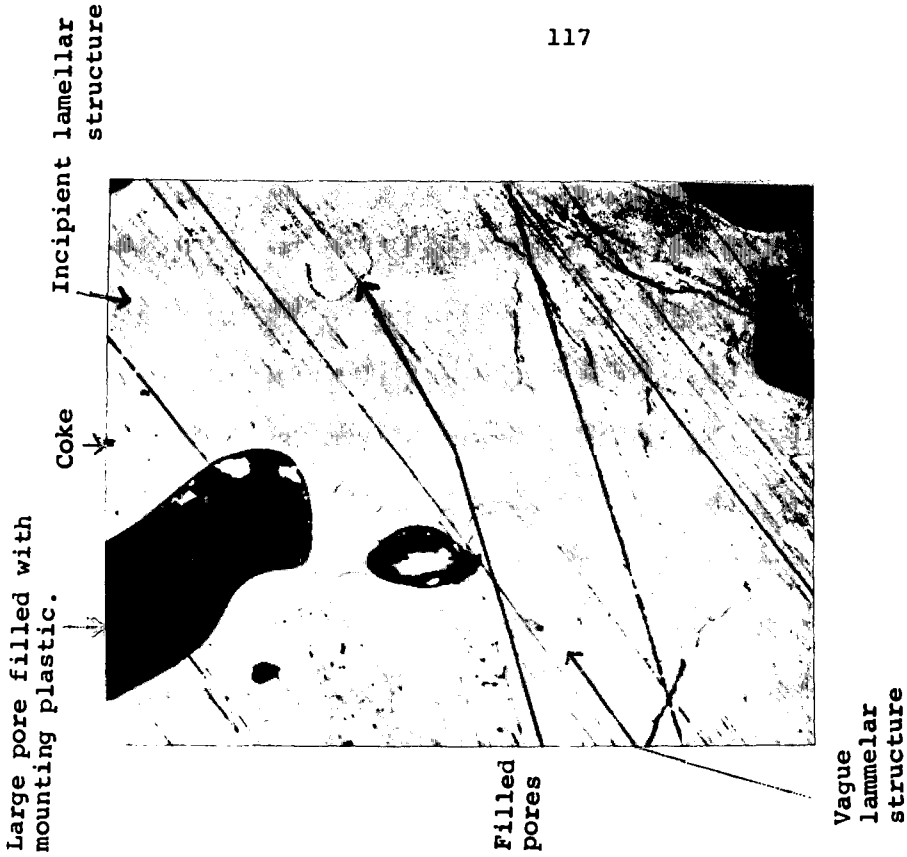
Figure 2
Green Delayed Coke P
100X

Incipient lamellar structure

Coke

Large pore filled with mounting plastic.

Filled pores

Vague lammelar structure

COMMERCIAL ANODE MIX
-4 MESH + PAN AGGREGATE

MIXING TEMP. 160°C
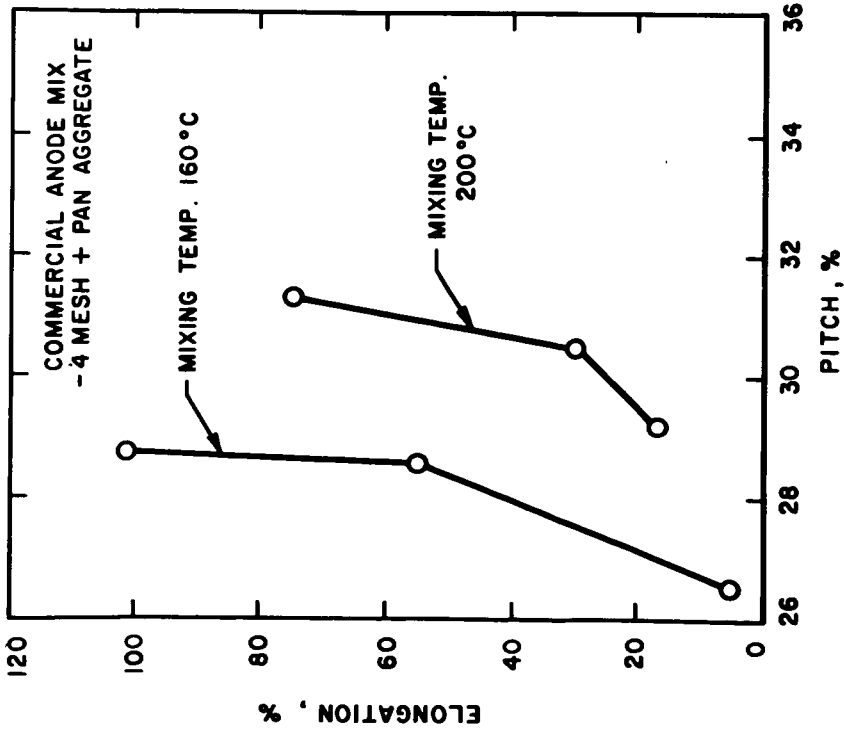
MIXING TEMP. 200°C

EFFECT OF MIXING TEMPERATURE
ON ELONGATION

FIG. I
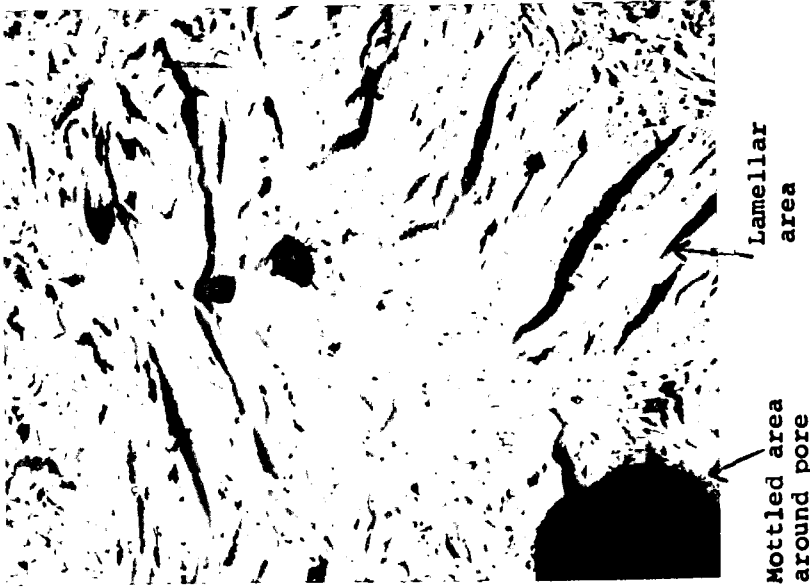
Figure 4

Calcined Delayed Coke W
100x
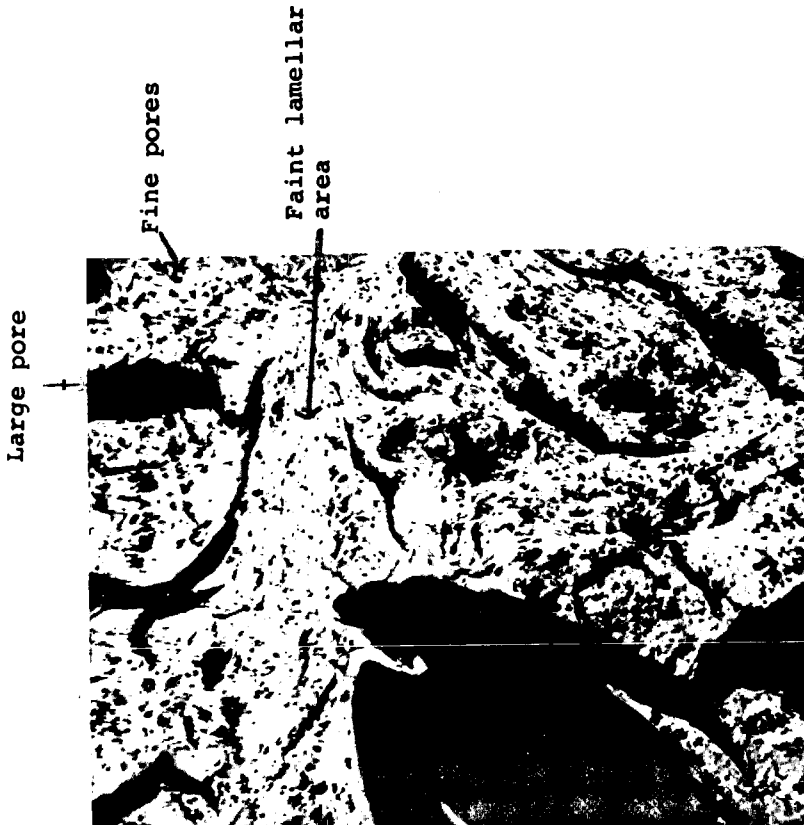
Figure 3

Calcined Delayed Coke P
100x

Cluster of spherules

Onion structure

Figure 6

Fluid Coke F Baked in Laboratory
100X

Surface coating

Spheres with onion structures

"Binder" coke

Figure 5

Calcined Delayed Coke G
100X

Interface between Coke G and binder coke.

Figure 8 - Laboratory Soderberg Anode Containing 46-1/2% of Coke G (100C)

Separation between Coke F and binder

Coke F - half coated with binder

Coke F no binder coating

Binder and Coke P Fines

Coke F cell wall
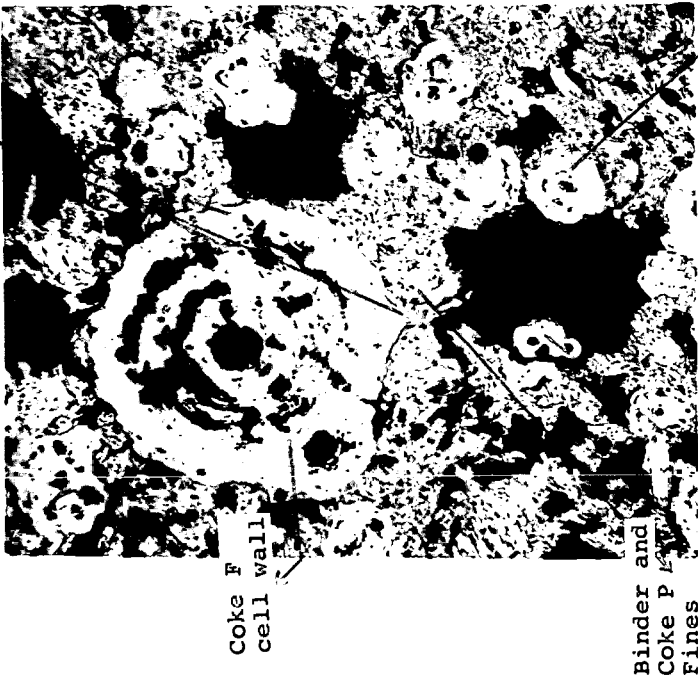
Figure 7 - Laboratory Soderberg Anode Containing 20% Coke F (100X)

PETROLEUM COKE HANDLING PROBLEMS

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INTRODUCTION

Calcined petroleum coke is an industrial carbon which is used
as a raw material in the Aluminum Industry and the Graphite Industry.
From the time it is first formed as a by-product of petroleum refining
until it is finally processed into elemental carbon it is handled many
times. Extreme care must be exercised at each point of handling in
order to preserve the desired physical structure and maintain the re-
quired degree of purity. This paper reviews the steps used in the
carbon industry to achieve these objectives.

Quality Considerations

Calcined petroleum coke is a commodity which must be delivered
to the ultimate consumer in a size range which will permit an adequate
proportion of coarse particles. This is necessary in order to meet
the formulation requirements in a carbon paste mix. It must also be
free from contamination.

Formation of Petroleum Coke

Raw petroleum coke is a by-product from refining of petroleum
residuals. One of the procedures by which this is accomplished is
known as the delayed coking process. This gives a coke with a sponge-
like structure. Other methods such as the fluid coking process are
also used but the product from this operation does not have the struct-
ural properties required for use in the Aluminum Industry or Graphite
Electrode Industry.

Figure 1 shows a cross section of a coke drum and illustrates
how the coke is formed in the delayed coking operation. The drum is a
large insulated vessel about 20 feet in diameter and 70 feet high. The
coke is formed at the rate of about 2 feet per hour and proceedes to
build up during a 24 hour cycle. The material at the bottom is fully
polymerized and develops a porous structure through which gases and
liquids can pass. The top layer in the coke drum is not fully poly-
merized until it is subjected to heat for a prolonged period of time.

At the very top, some foam occurs. This foam subsides during the steaming and cooling cycle. It is important in filling the coke drum to avoid any carry over of foam or pitchy material into the vapor lines. Foam depressants are used to minimize the amount of foam (1). Level indicators are used to establish the position of the liquid or foam in the drum (2). These are operated by transmitting a beam from a radioactive source to an instrument mounted near the top of the drum. When the liquid reaches a predetermined level the feed to the drum is switched to an empty drum. At this time the full drum is steamed to remove light hydrocarbons and finally cooled by introducing water at the bottom of the drum.

Factors affecting Sizing of Coke

The coke is removed from the drum by means of high pressure water jets which operate on the principle used in hydraulic mining of coal (3). The procedure used in cutting the coke from the drum is extremely important. If it is not carried out properly the physical structure of the coke will be destroyed and the ultimate consumer would not have enough coarse particles to balance out their carbon aggregate formulation. The recommended procedure for cutting the coke is illustrated in Figure 2. This series of diagrams shows the steps which should be taken in order to get the maximum amount of lump coke needed for further processing.

The first step is to bore a pilot hole. During this operation the fine cuttings are held in the upper section of the drum until the hole is completely through the bottom. At this time, all of the center cuttings fall out of the drum together with the water used in cutting.

The drill stem is raised to the top and the bit is changed to a cutting head which has nozzles directed in a horizontal manner. The pilot hole is enlarged so that lumps of dislodged coke can fall freely through the opening. This avoids the danger of a coke build up around the drill stem which would prevent the rotation of the cutting head.

Once the pilot hole is enlarged the stem is raised to the level of the coke in the drum. The operator can tell by the sound of the water hitting the metal walls when the top is reached. At this time the stem is lowered 3 - 4 feet below the top. It is held in this position for several minutes until the coke is undercut. Then the stem is raised and lowered rapidly within this section until the coke is all cut from this layer. This action causes the coke to collapse from the drum walls resulting in large pieces which fall through the pilot hole. This operation is repeated until the drum is completely empty. In general, the decoking operation requires about 3 to 4 hours depending on the hardness of the coke. The harder

the coke the more time required.

Lump coke in the size range of baseballs to footballs can be handled easily in conventional conveying systems. At the calcining plant all coke is run through a roll crusher set at an opening of 4 inches before it is fed to the kiln. The tumbling action in the kiln results in further degradation so that the final product all passes a 1 inch screen with approximately 35 to 40% retained on a ¼ inch screen.

Procedures to avoid Contamination

There are several systems used in handling coke after it is discharged from the drum. These are as follows:

A. The coker is mounted over a railroad track so that coke can be discharged directly into open hopper cars or gondola cars.

B. A roll crusher is placed below the drum on small tracks. This breaks up the large lumps to a size which will permit a coke slurry to be transported by pumping through a pipe line.

C. The coke is directed to a ramp which leads to a pit. The pit may or may not contain water for further cooling of the coke.

In each of the above systems it is necessary to provide for the recovery of water used in cutting. The areas around the coking unit should be paved. Curbs and retaining walls should be provided to contain any coke spillage. The drainage around the coker must be carefully planned to avoid sand, clay and gravel from entering the system. Drainage from rainstorms should be directed away from the coking unit.

Transporting and Conveying Coke

The freight cars used to transport the coke should be clean. Any sand, gravel or iron rust will contaminate the coke. The cars should be carefully inspected before loading.

When coke is unloaded at the calcining plant, it is either conveyed directly to a storage silo or to an outdoor storage. When outdoor storage is necessary, it is preferable to provide paved areas to minimize contamination. The activities in the surrounding area can also affect the purity of the coke. For example, unloading of iron ore in the vicinity will contaminate the coke pile under

certain wind conditions.

Magnetic separators are used at the calcining plants. These will remove scrap iron from green coke, but will not remove iron rust, since the latter is non-magnetic. During calcining any iron oxide (rust) will be reduced to iron which can be removed from the calcined petroleum coke with magnets.

Chemical Composition of Petroleum Coke

Green petroleum coke from the delayed coking process is essentially a hydrocarbon. The chemical composition as obtained by an ultimate analysis is given in Table I. Before it can be used as a carbon aggregate it is necessary to convert the green coke into elemental carbon by a petrochemical process. This is carried out by a pyrolytic treatment at temperatures around 2300°F. In this operation the carbon is not developed until hydrogen is chemically removed by thermal decomposition. In the trade this process is referred to as calcination, but it is essentially a dehydrogenation reaction which converts a hydrocarbon into elemental carbon as indicated in Table I.

A number of changes in basic properties and structure are brought about by the removal of chemically bound hydrogen from the hydrocarbons in order to produce elemental carbon. Some of these are as follows:

A. The real density of green petroleum coke is 1.30. After calcining the real density is 2.07.

B. Green petroleum coke is an electrical insulator whereas elemental carbon (calcined petroleum coke) is an electrical conductor. For example:

Electrical Resistivity of Green Petroleum coke is 9×10^6 ohm-inches.

Electrical Resistivity of Calcined Petroleum coke is .035 ohm-inches.

C. There are corresponding changes in the X-ray diffraction pattern.

While there are profound changes occurring during the chemical conversion of green petroleum coke to elemental carbon, the mineral matter as indicated by the ash content remains essentially unchanged. The composition of the ash is important as this will affect the type of aluminum metal which can be produced.

The metallic components which are present in the crude oil will be carried over into the coke. Materials such as vanadium and nickel occur in crude oils in varying amounts depending on the area of origin. There is actually very little if any iron or silicon in crude oil. Iron which is found in petroleum coke comes primarily from corrosion of the pipes and vessels used to process the crude oil. Additional iron finds its way into the coke in the form of rust from rail cars and conveying equipment. Silicon can come from the catalyst used in refining also from sand or gravel contamination.

Iron and Silicon in Calcined Petroleum Coke

The iron in calcined petroleum coke will normally range between .01 and .06%. The silicon content will range between .01 and .05. Table II shows the car analysis of iron and silicon in calcined petroleum coke all loaded from the same storage silo. The samples were taken from a conveyor belt with an automatic sampler. In this group of cars, we find some individual cars with iron as low as .019% and silicon as low as .010%. This information is useful to the carbon plant superintendent of a prebaked plant. If he is required to supply anodes which are low in iron or silicon, he can select the cars from a given shipment and segregate the low ash material in a separate area of his storage shed.

Since the iron in calcined coke is magnetic, further removal can be accomplished at the consumers' plant by using magnetic separators. This will be most effective if applied after the grinding operation since iron pick up does take place in equipment such as the ball mill.

Several aluminum plants are now asking for a special grade of carbon with very low silicon. This is a difficult requirement to control at an ordinary calcining plant. However, a substantial improvement can be accomplished by screening the coke and using the coarse fraction for the low silicon application. An example of the degree of improvement which can be achieved by this method is shown in Table III. The silicon bearing material is concentrated in the fines (minus ¼"). The plus ¼" fraction contains only 40% of the total silicon or .008%.

SUMMARY

In summarizing the information just presented, we find that a reasonable amount of care should be exercised at each step of handling petroleum coke. It is recongnized that some of the physical properties (sizing) of a calcined coke can be destroyed if the cutting operation is not carried out properly. Also sources of contamination should be avoided in order to keep the iron and silicon content within required limits. Where a carbon aggregate with low silicon or low iron is required a selection can be made from a given shipment if the material is delivered in rail cars.

References

1.   Trammell, W. D., Glaser, D., Oil and Gas Journal p. 65, June 5, 1961.

2.   Wright, P. G., Oil and Gas Journal p. 93 - 94, Aug. 11, 1958.

3.   Maas, R., Lauterbach, R. E., Petroleum Engineer p. 110 - 124, Feb. 1947.

VAPOR OUT

835 °F.
70 PSIG.

VAPOR
$\rho = 1$ LB./FT.^{3}

$\rho = 9$ LB./FT.^{3}

FROTH

10 FT.

$\rho = 13$ LB./FT.^{3} $\rho = 18$ LB./FT.^{3}

$\rho = 45$ LB./FT.^{3}

$\rho = 55$ LB./FT.^{3}
COKE

CHARGE FROM
DELAYED COKER
HEATER
12,000 B/D , 910 °F.
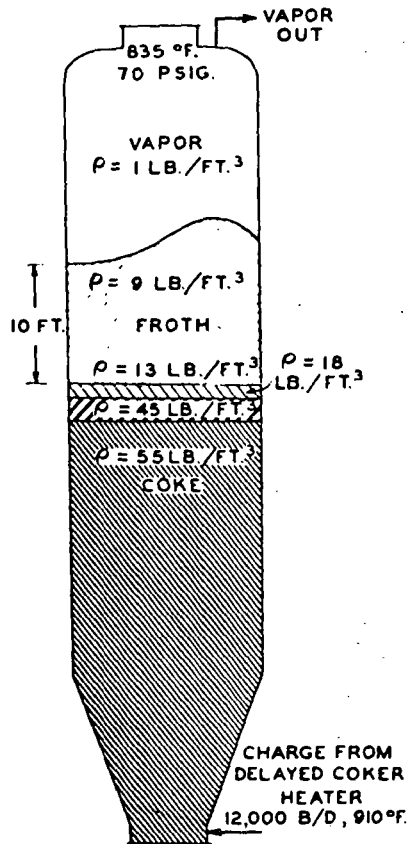
Figure 1.

Figure 2

RECOMMENDED DECOKING PROCEDURE

STEP 1

DRILL PILOT HOLE

STEP 2

USE CUTTING BIT TO ENLARGE PILOT HOLE

STEP 3

LOWER BIT 3 Ft. BELOW TOP COKE HOLD UNTIL COKE IS UNDERCUT

STEP 4

RAISE AND LOWER BIT RAPIDLY CAUSING COKE TO COLLAPSE FROM WALLS.
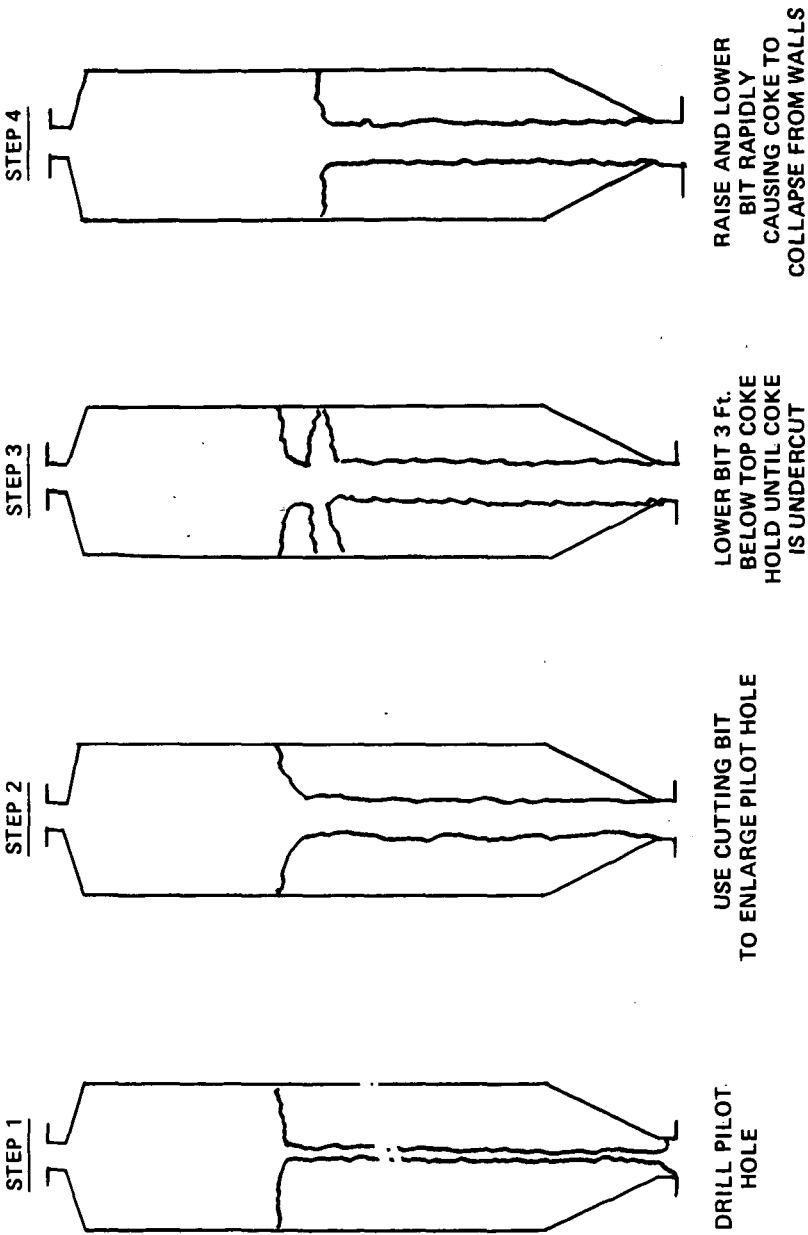
STEP 5 – REPEAT STEPS 3 AND 4 UNTIL DRUM IS EMPTY

STEP 6 – CLEAN DRUM WALLS

TABLE I

TYPICAL ULTIMATE ANALYSIS OF
GREEN PETROLEUM COKE AND CALCINED PETROLEUM COKE

	Green Petroleum Coke (Polymerized Residual)	Calcined Petroleum Coke (Pure Carbon)
CARBON	91.80	98.40
HYDROGEN	3.82	0.14
OXYGEN	1.30	0.02
NITROGEN	0.95	0.22
SULFUR	1.29	1.20
ASH	0.35	0.35
CARBON-HYDROGEN RATIO	24	910

TABLE II

ANALYSIS OF CALCINED COKE SHIPMENTS
CARS LOADED FROM PRODUCT SILO

ORDER OF LOADING CAR NO.	ASH %	IRON %	SILICON %
1	.24	.019	.010
2	.21	.021	.012
3	.40	.065	.028
4	.42	.073	.022
5	.34	.043	.025
6	.24	.030	.010
7	.23	.020	.015
8	.33	.035	.025
9	.41	.065	.015
10	.26	.041	.021

TABLE III

EFFECT OF SCREENING
ON SILICON CONTENT OF
CALCINED PETROLEUM COKE

SIZE	% SILICON
Run of Kiln	.021
Plus ¼ Inch Fraction	.008
Minus ¼ Inch Fraction	.022

COKING OF COAL SOLUTIONS IN A
LABORATORY COKE OVEN

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INTRODUCTION

The manufacture of aluminum by the Hall-Heroult process requires nearly one-half pound of high-grade carbon for each pound of aluminum produced. This carbon must contain a minimum of metallic impurities to prevent contamination of the aluminum produced in the process. For this reason raw materials used in the anode manufacture for the aluminum industry have stringent purity specifications. Petroleum coke represents a large volume source of relatively pure carbon and is used extensively throughout the aluminum industry as the material of choice for anode manufacture.

Most of the petroleum coke that is used in electrode manufacture is produced in delayed cokers where the product is subsequently calcined in rotary kilns to temperatures of 1200°C — 1430°C[1]. After heat treatment to this temperature the coke has obtained dimensional stability and electrical conductivity suitable for its use as an electrode material. Coke produced by this process usually has a particle size adequate for its use in the manufacture of large monolithic electrodes. A limited amount of petroleum coke produced in fluid bed cokers is used in the manufacture of anodes for the aluminum process. Fluid coke is sometimes used as a supplement to delayed petroleum coke to produce electrodes. The absence of large size particles in fluid coke generally limit its use in large electrodes. A limited amount of coke is produced for electrode use by the delayed coking of Gilsonite[2]. Recently, the Nittetsu Chemical Industry of Japan completed the installation of a delayed coker for the coking of coal tar pitch for electrode use[3,4]. Some coal tar pitch coke is manufactured in Europe to supplement the supply of petroleum coke. This coke is generally produced in coke ovens[5].

Coke derived from coal had not been used as a general source of anode carbon in alumina reduction cells because of its high ash content. Investigators have studied methods of removing mineral matter from coal,[6-11] and coke from purified coal has been used on a commercial scale in at least two cases[12-14]. These were war-time uses that were discontinued when adequate supplies of high-grade petroleum coke were available.

Because of possible future shortages of electrode grade petroleum coke, we have studied the coking of purified solutions of coal in creosote oil as a process for producing an alternate source of electrode grade coke. A pilot plant was constructed at Reduction Research Laboratory where high-volatile bituminous coal was mixed with heavy residue creosote oil and digested under pressure to give a solution of coal. The solution was treated with a combination

of disc and solid bowl centrifuges to yield a solution of coal that had been freed from its mineral matter and fusain. Most of the solvent oil was removed from the coal by distillation in a continuous still and the pitch-like residue remaining from the distillation was charged as a liquid to a coke oven where the remaining solvent and volatile matter were removed to produce a calcined electrode grade coke[15]. The principal process steps are shown diagrammatically in Figure 1. This paper will be concerned primarily with our experience in operating a laboratory coke oven to produce calcined coke.

While much excellent work has been published on the solubility of coal in different solvents[15-23], little has been published about coking of such solutions to yield coke. We were aware that most of the petroleum coke was produced in delayed cokers and that Gilsonite was being coked in delayed cokers to produce a high-grade electrode coke, but we were uncertain that a product as aromatic as dissolved coal could be satisfactorily handled in a delayed coker. The Koppers Company in the United States had coked coal tar pitch in coke ovens; coke ovens are being used to coke coal tar pitch in Russia[24] and Germany; and we were aware that the coal solution produced in the Pott-Broche process in Germany during World War II had been coked in slot ovens[13].

The product of a delayed coker is not satisfactory for use in an alumina reduction cell without further heat treatment to remove the residual volatile matter, obtain proper electrical conductivity, and insure dimensional stability of the coke particles at high temperature. Generally, the coke from the delayed coker is heat treated or calcined to a temperature of about 1300°C before use in alumina reduction cell anodes. Thus, the use of a delayed coker would also require the use of a calciner. We elected to combine the two steps in our pilot plant and construct the only coker that we knew of capable of operating at temperatures of 1300°C - the coke oven.

PROCESS DESCRIPTION

The Bureau of Mines had reported[25] on a coke oven heated with silicon carbide glow bars of the approximate size that we needed. We used the general idea of this coke oven as our model, with the exception that the coke oven we constructed was gas fired and the sole of the oven was heated by the passage of hot gas from the flue to the exhaust stack. The oven was fired symmetrically with burners at four corners of the flues, and the flues were baffled to provide uniform heat distribution for the entire surface of the refractory. The coking slot was 17 inches wide by 48 inches long by 48 inches high and was tapered one-quarter inch from the pusher end to the coke end over the length of the slot. The slot walls were silica refractory of the type used in commercial coke ovens while the sole was super-duty fire-clay refractory. The roof and doors were cast with super-duty castable refractory. Tongue and groove construction was used to maintain better seals in the refractory joints. The oven was fired with four 158,000 Btu per hour capacity gas burners. The system was protected against high and low gas pressure and blower failure. Because the refractories were incandescent during operation, flame failure protection was regarded as superfluous. Figures 2 and 3 are diagrammatic sections through the coke oven.

Cokes from the solution of two different coals were studied in the coke oven. Both of these coals were high volatile bituminous coals. One was the Black Creek Seam in Northern Alabama and the other, the No. 9 Seam in Western Kentucky. Typical analysis of these coals are shown in Table 1. Prior to each charging, the door faces were cleaned, seated on a strand of asbestos rope and sealed with a refractory cement.

Steam was introduced into the oven slot to reduce the surface temperature of the refractories before charging the dissolved coal to the oven. This was done to minimize the amount of carbon-black formed by cracking of the coal solution on the incandescent refractory surfaces. After passing through the continuous still where part of the solvent was removed by distillation, the dissolved coal solution was fed into the top of the coking slot and the volatile matter and gases that were flash evaporated were passed through a condenser. The condensed vapor was collected in a solvent recovery tank where it was recombined with the solvent fractions removed by the continuous still.

The hot coal solution was charged at a rate of about 2 — 3 gallons per minute into the slot of the coke oven. While this material left the still at about 320°C, it had cooled to about 200°C in the piping by the time it had reached the coke oven. During the first few minutes of the charge the condenser was flushed with a spray of water to wash away the copious quantities of carbon-black that were generated. When the first condensation of oil was observed, the water spray was discontinued in the condenser, and the condensing oil was turned into the solvent recovery tank. At this point the flow rate was reduced to about 1 gallon per minute. At a predetermined volume, usually 300 gallons, the feed rate to the coke oven was decreased to about 0.5 gallon per minute for the remainder of the usual 400 gallon charge. At that point the coke oven was removed from the feed circuit and the lines and still were flushed with recovered oil. The oven was observed for about one hour after the completion of the charge for excessive frothing.

Malfunctions in the operation, such as oven door leakage or excess oven pressure, were corrected as they occurred. If care was taken to clean the condenser and prevent excess pressure from developing in the oven, the carbon-black formed at the beginning of the charge soon sealed the doors and cracks in the flues, and the operation settled down to a relatively smoke-free condition. Figure 4 illustrates typical temperature cycles during the operation of the coke oven.

After completion of the charge, the coke was held in the oven for an additional 8 — 10 hours to permit the coke to obtain a uniform temperature of 1250°C — 1300°C. This temperature was measured with an optical pyrometer on the coke surface through an observation port in the top of the furnace. Before any work was done on the oven, a valve was closed between the condenser and the receiver tank. This was done to prevent hot gases and sparks from the oven from igniting any accumulated combustible gases in the tank.

At the completion of the coking cycle, the doors were lifted and the coke was pushed from the oven with a mechanical ram. During pushing the coke was quenched slightly with water and permitted to evaporate to dryness. As removed from the oven the coke was in large strong, angular lumps with some anisotropic

structure. Properties of the cokes compared with that of a typical petroleum coke are shown in Table II. Use of the coke in anodes of commercial reduction cells showed the coke to be satisfactory in every respect[26].

DISCUSSION

As the gases from the coke oven were vented to the atmosphere and the liquid product recombined with the solvent oil removed by distillation, it was not practical to obtain a material balance on the coking operation. However, work done by the Bureau of Mines from the coking of the Black Creek coal in retorts at 1000°[27] provides some insight into the product distribution that could be expected from this coal on carbonization. This information is shown in Table III along with the coke yield from a series of coke oven runs involving some 20 tons of coal from the Black Creek Seam. About 44 percent of the original coal is converted to calcined coke that would be usable in aluminum cell anodes. The coke obtained from coking the purified coal solution, when combined with the coke obtained from coking the centrifuge sludge, agrees within about 2 percent of the amount of coke predicted by the Bureau of Mines for this particular coal. This would indicate that the molecular size distribution of the coal has not been greatly altered by solution.

Normally, when we open the coke oven doors, we found that the coke charge had shrunk and pulled away from the coke oven walls. The charge could be pushed from the oven with very little effort. In some cases when it was necessary to interrupt the charge to the coke oven for any prolonged length of time (two hours) we found that the coke charge was stuck tightly to the oven wall and we were unable to remove the coke with the pusher. In these cases it was necessary to break the coke from the oven with steel bars. We adopted the practice of charging the solution to the oven continuously and if we were forced to interrupt our charge sequence for more than an hour we terminated the charge at that point and coked a partially filled oven.

Our experience has shown that we can produce a satisfactory electrode coke from high-volatile bituminous coal through a solution process followed by coking in a slot-type coke oven.

ACKNOWLEDGMENT

REFERENCES

1. Scott, C. B., "Petroleum Coke as a Raw Material for Graphite and Metallurgical Carbon Manufacture," Chemistry and Industry, July 1, 1967, pp 1124-1131.

2. Kretchman, H. F., The Story of Gilsonite, American Gilsonite Company, Salt Lake City, Utah, 1957.

3.   Chemical Week, November 30, 1968, pp. 41-45.

4.   Gambro, A. J., D. T. Shedd, H. W. Wang and T. Yoshida, "Delayed Coking of Coal Tar Pitch," paper presented to American Institute of Chemical Engineers, New Orleans, La., March, 1969.

5.   Osthaus, K. H., "The Porduction (sic) of Pitch Coke," Journal of Mines, Metals and Fuels (India), 1959 (Special), pp. 334-336.

6.   Selvig, W. A., W. H. Ode, and F. H. Gibson, "Coke from Low-Ash Appalachian Coals for Carbon Electrodes in Aluminum Industry," Bureau of Mines Report of Investigations 3731, 1943, 188 pp.

7.   Graham, H. G., and L. D. Schmidt, "Methods of Producing Ultra-Clean Coal for Electrode Carbon in Germany," Bureau of Mines Information Circular 7481, 1948, 13 pp.

8.   Campbell, R. J., Jr., R. J. Hilton, and C. L. Boyd, "Coal as a Source of Electrode Carbon in Aluminum Production," Bureau of Mines, Report of Investigations 5191, 1956, 53 pp.

9.   Klemgard, E. N., "Electrode Carbon from Washington State Coal," Bulletin No. 218, Washington State Institute of Technology, Pullman, Washington, 1953, 37 pp.

10. Bloomer, W. J., and F. L. Shea, "Coal Deashing and High-Purity Coke," American Chemical Society, Division of Fuel Chemistry, Preprints, 11 No. 2, 378-392 (April 1967).

11. Kloepper, Dean L., Thomas F. Rogers, Charles H. Wright, and Willard C. Bull, "Solvent Processing of Coal to Produce a De-ashed Product," Research and Development Report No. 9, Office of Coal Research.

12. Nelson, H., "The Selective Separation of Super Low Ash Coal by Flotation," Gas World, Vol. 127, 1947, pp. 125-130-132.

13. Lowry, H. H., and H. J. Rose, "Pott-Broche Coal Extraction Process and Plant of Ruhrol G. M. B. H., Bottrop-Wilheim, Germany," Bureau of Mines Information Circular 7420, 12 pp.

14. Graham, H. G. and L. D. Schmidt, "Methods of Producing Ultra-Clean Coal for Electrode Carbon in Germany," Bureau of Mines Information Circular 7420, 12 pp.

15. Bullough, V. L. and W. C. Schroeder, U. S. Patent 3,240,566.

16. Dreyden, I. G. C., British Coal Utilization Research Association Monthly Bulletin, Vol. XIII, Nos. 4 and 5, 1949, pp. 113-138.

17. Golombic, C., J. B. Anderson, M. Orchin, and H. H. Storch, "Solvent Extraction of Coal by Aromatic Compounds at Atmospheric Pressure," Bureau of Mines Report of Investigations 4662, 1950, 12 pp.

18. D'yakova, M. K., A. V. Lozoyi, T. G. Slepantsera, and S. A. Senjavin, "Solutions of Coals," Compt. rend. Acad. Sci., U. S. S. R., Vol. 20, 1938, pp. 681-4, (in English.).

19. Kostal, J., "Extraction of Coal Under Pressure," Prace ustavu pro uyzkum a vyuziti paliv 8, pp. 60-85, 1957 (in Czech.).

20. Srinevasan, S. R., N. G. Basak, and A. Lahiri, "Pressure Extraction of Vitrain-rich Coal with Anthracene Oil," J. Sci., Industr. Res. (India), Vol. 19B, Jan., 1960, pp. 10-15.

21. Lahari, A., and A. N. Basu, "Improvements in or Relating to the Solvent Extraction of Coal," Indian Patent No. 49, 729, Dec. 14, 1954.

22. Rose, H. J., and W. H. Hill, "Coal-Treatment Process," U. S. Patent 1,923,005, August 29, 1933.

23. Van Krevelen, D. W. and I. Schuyler, Coal Science, Elsevier, 1957, Chap. 3.

24. Dobrovolski, I. P., M. V. Donde, and N. Kh. Nemirovskii, "Some Problems in the Planning and Running of Pitch Coke Plants," Coke and Chemistry, U. S. S. R., Vol. 1, 1961, pp. 30-33.

25. Gayle, J. B., and H. S. Auvil, "Development of New, Experimental Coke Oven," Bureau of Mines, Report of Investigations 4923, 1952, 17 pp.

26. Bullough, V. L., L. O. Daley, W. R. Johnson and C. J. McMinn, "Electrode Tests of Purified Coke from Coal in Aluminum Manufacture," American Chemical Society, Division of Fuel Chemistry, preprints, 12 No. 4, 73-80 (September, 1968).

27. Fieldner, A. C., J. D. Davis, R. Thiessen, E. B. Keister, W. A. Selvig, D. A. Reynolds, F. W. Jung, and G. C. Sprunk, "Carbonizing Properties and Constitution of Black Creek Bed Coal From Empire Mine, Walker County, Alabama," Bureau of Mines Technical Paper 531, 1932, 67 pp.
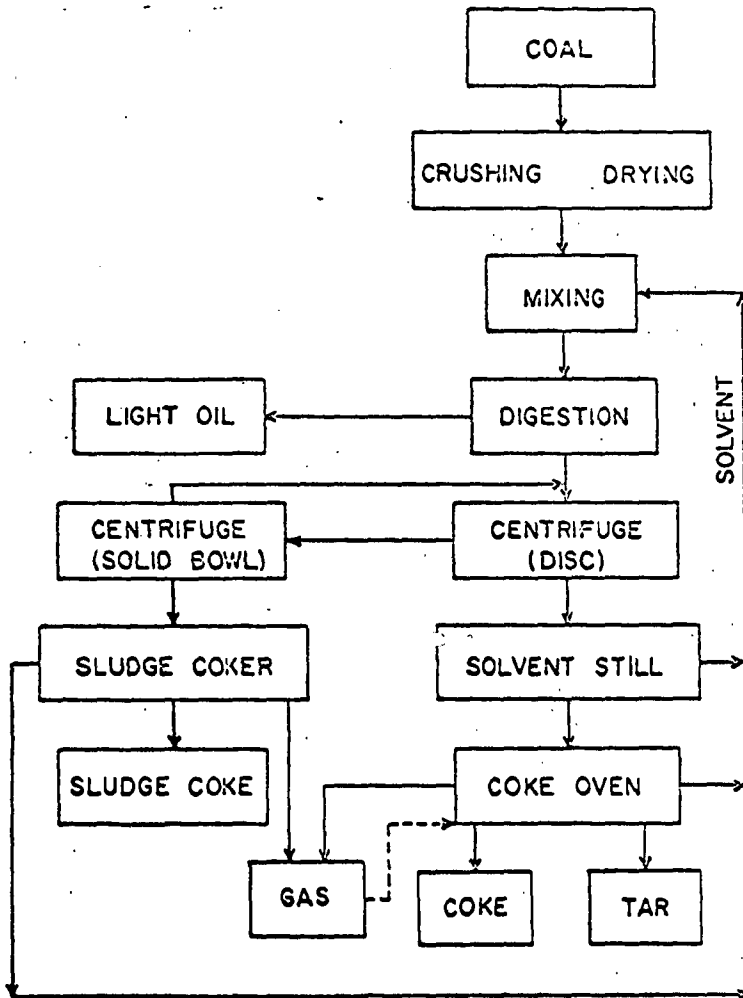
FIGURE 1. DIAGRAM OF A COKE-FROM-COAL PROCESS

TABLE I.

ANALYSES OF COALS USED IN INVESTIGATION OF ELECTRODE COKE FROM COAL

	Black Creek Coal Seam		Kentucky No. 9 Coal Seam	
	As Received	Dry, Ash-Free	As Received	Dry, Ash-Free
Moisture	2.7	----	----	----
V. M.	35.4	37.4	40.5	45.0
Ash	2.8	----	9.9	----
H_2	5.4	5.4	5.1	5.6
C	79.8	84.4	72.5	80.5
N_2	1.7	1.8	1.5	1.7
O_2	9.5	7.6	7.9	8.8
S	.8	.8	3.1	3.4
Anthraxylon		45		65
Trans. Attritus		38		27
Opaque Attritus		7		5
Fusain		10		3
B. t. u.	14,310	15,150	13.060	14,500

Source: Bureau of Mines. Bull. 550.

TABLE II.

PROPERTIES OF COKES FROM KENTUCKY COAL AND
ALABAMA COAL AFTER CALCINING TO 1340°C

	Alabama Coke	Kentucky Coke	Typical Petroleum Coke
Specific Gravity	2.02	2.01	2.03
Electrical Resistivity, ohm-in.	0.029	0.034	0.034
Hardgrove Grindability Index	22	22.5	37
Sulfur, Percent	0.46	0.67	0.8 - 1.65
Silicon, Percent	0.04	0.09	0.03
Iron, Percent	0.07	0.08	0.05
Aluminum, Percent	0.09	0.09	0.02
Ash, Percent	0.58	0.76	0.34

INSULATION

SILICA REFRACTORY

FIRECLAY REFRACTORY
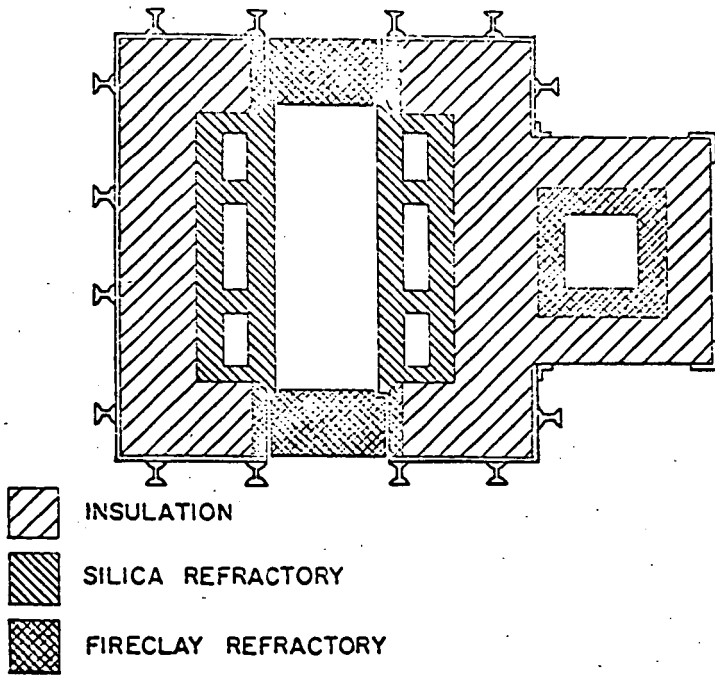
FIGURE 2. EXPERIMENTAL COKE OVEN TYPICAL CROSS SECTION THROUGH FLUES AND COKE CHAMBER (VIEWED FROM ABOVE)
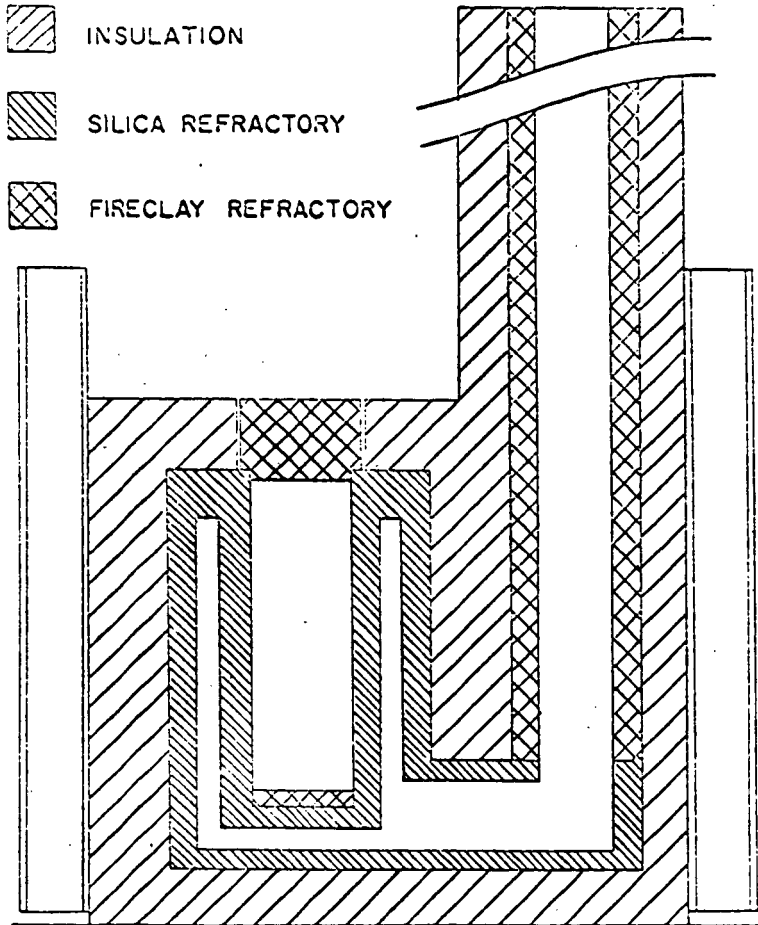
FIGURE 3.   EXPERIMENTAL COKE OVEN – TYPICAL CROSS
SECTION THROUGH FLUES AND COKE CHAMBER
(VIEWED FROM COKE END)
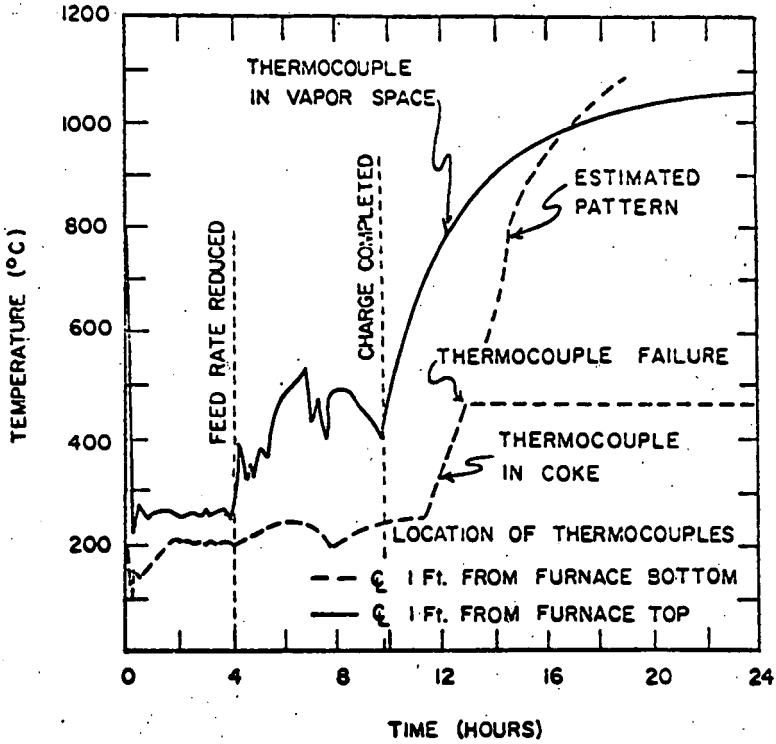
FIGURE 4.   TEMPERATURE PATTERN IN COKE
             SLOT DURING COKING

TABLE III.

PRODUCT YIELD FROM COKING OF
BLACK CREEK COAL

	Estimated[1]	Found
COKE	66.6%	44.2%
CENTRIFUGE RESIDUE COKE	----	24.4%
GAS	17.6%	----
TAR LIQUOR	6.7%	----
AMMONIA	0.2%	----
TAR	6.0%	----
LIGHT OIL	1.3%	----

[1]Fieldner, A. C., et. al., Bureau of Mines Technical Paper 531, 1932.

PEABODY CONTINUOUS COKING PROCESS

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ABSTRACT

The paper presents a description of the Peabody Continuous Coking Process which produces coke from coal in a continuous operation. Carbonization is initiated on a moving bed grate carbonizer. A controlled flow of preheated air at 450°F is percolated through the moving bed. Retention time in this pre-treatment furnace is normally about 18 minutes. The product from the moving bed containing 7-10% volatile matter is discharged to a shaft furnace where de-volatilization is completed. The hot coke product from the shaft furnace is cooled with inert gas which is generated in the process. By-product gas from the moving bed carbonizer and shaft furnace are combined and used as energy for steam generation or for other purposes. Utilization of the by-product energy is essential to the economics of the process.

INTRODUCTION

The original development work on carbonization of coal on a moving bed furnace was done by Mr. A. H. Andersen of Shawinigan Chemicals, Ltd. at Shawinigan Falls, Quebec in the late 1930's. During the pre-war period, Shawinigan put into operation a number of moving bed carbonizers to produce coke for use in carbide furnaces.

Study of this original work and test reports on a similar installation in South Africa in the middle 1950's indicated certain limitations as to the size of

coal that could be carbonized on a moving bed carbonizer without excessive burning of fixed carbon at the expense of coke yield.

In 1957 Peabody Coal initiated the research and development that resulted in combining a moving bed carbonizer with a shaft furnace. Early test work indicated that to make a totally enclosed continuous system, inert gas cooling or quenching of the product was required to prevent air pollution.

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1. Andersen, A. H. and N. R. Fasken

    Carbonization. U. S. Pat. 2,380,930

    August 7, 1945

    Andersen, A. H. and J. E. Renaud

    Coke Production. U. S. Pat. 2,209,255

    July 23, 1940

2. LaGrange, C. C. Journal of the South African Inst. of Mining

    & Metallurgy

    October, 1956 v 57 No. 3 pp 99-114

DESCRIPTION OF PROCESS

Figure I shows a flow sheet of the continuous coking process. Coal is fed uniformly by a layer loader onto a moving bed grate carbonizer where the coal is subjected to a furnace environment of 1800°F to 2000°F. Ignition of the coal is automatic as it enters the furnace on the top layer of the coal bed. Carbonization through the plastic state proceeds downward as a controlled amount of preheated air (450°F) is percolated upward through the moving bed. Retention time in this pretreatment furnace is normally 18 minutes and timed to prevent over-carbonization of the top layer of coal.
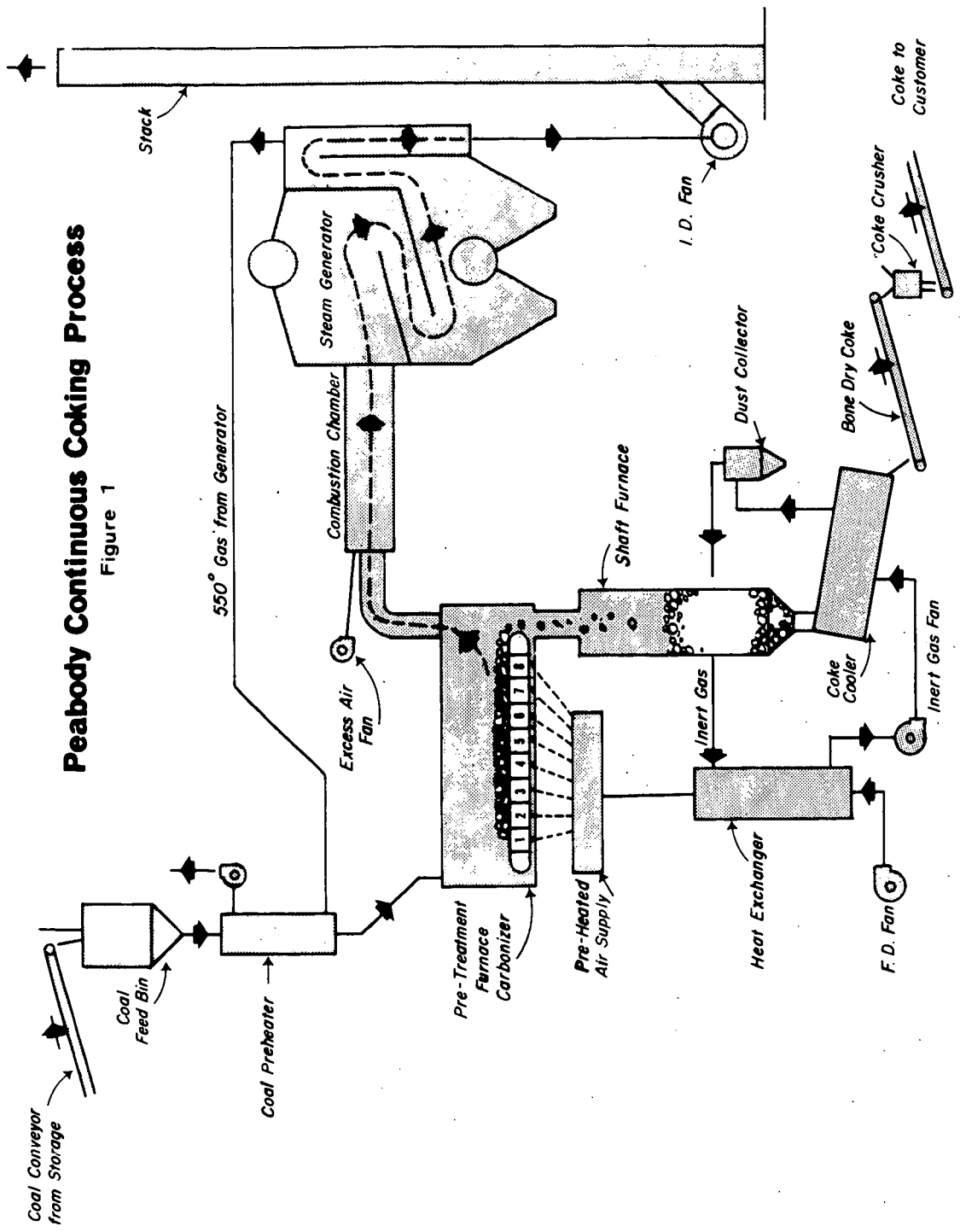
To prevent excessive carbonization of the top layers, the timing and the amount of preheated air is controlled so that 7% to 10% volatile still remains in the product as it is discharged into the shaft furnace. Devolatilization is completed in the shaft furnace without air by retention of the product in the shaft furnace for one hour.

At the bottom end of the shaft furnace the hot coke product (1600°F to 1800°F) is discharged by gravity into an inert gas cooling unit where the coke product is cooled to a temperature of 250°F. The inert gas is self-generated in the combined shaft furnace and cooling system. This system is totally enclosed and prevents air pollution from dust particles or gases.

The by-product gas generated in the moving bed carbonizer and the shaft furnace are combined as an energy supply for steam generation or for other heat-using processes. The use of the by-product gas (approximately equivalent to CO gas) is essential to the economics of the process, particularly with high volatile coals.

Peabody Continuous Coking Process

Figure 1

Coal Conveyor from Storage

Coal Feed Bin

Coal Preheater

Pre-Treatment Furnace Carbonizer

Pre-Heated Air Supply

Heat Exchanger

F. D. Fan

Inert Gas

Inert Gas Fan

Coke Cooler

Bone Dry Coke

Coke Crusher

Dust Collector

Coke to Customer

I. D. Fan

Shaft Furnace

Combustion Chamber

Steam Generator

Excess Air Fan

550° Gas from Generator

Stack

TYPICAL ANALYSIS OF PRODUCT

FOR

ELECTRIC FURNACES

	Coal Input Chemical Analysis	Coke Output Chemical Analysis
% Fixed Carbon	54.59	89.52
% Ash	4.33	8.76
% Volatile	37.71	1.72
% Moisture	3.37	.00
% B.T.U.	13,965	13,035
% Sulfur	1.03	.90

Size	Screen Analysis Percent	Screen Analysis Percent
1 X 1-1/2	6.9	3.9
5/8 X1	21.5	11.7
1/2 X 5/8	14.2	23.6
1/4 X 1/2	32.0	53.3
-1/4	25.4	7.5

ENERGY BALANCE OF PEABODY PROCESS

	Input	Output
	M - B. T. U.	M - B. T. U.
Energy in Coal	27. 92	
Energy Reporting into Coke		15. 50
Energy Reporting into Steam		10. 44
Total Energy Recovered in Products		25. 94
Energy Conversion Efficiency		92. 9%

ECONOMICS OF THE PEABODY COKING PROCESS

Figure 2 was prepared from extensive tests and operating data obtained at the Columbia, Tennessee plant, which has been in continuous production for the past eight years. Capital cost data was based upon a 500-ton per day coke plant and the return on investment was calculated at 16% before taxes.

FLEXIBILITY OF THE PROCESS

1. The process variables of temperature, speed of carbonization, air to coal ratio, retention time, can be controlled over such a wide range of environment that practically all classes of coal can be carbonized.

2. The process can produce a bone dry coke product with a density range from 9 pounds per cubic foot to 32 pounds per cubic foot.

3. A blend of coals is not required to produce a suitable coke.

4. The continuous coking system is totally enclosed and can operate without dust or without objectionable air pollution.

Process Economics

Figure 2

COAL COST
Dollars per Ton
(F.O.B. Plant)

COKE COST (Dollars per Ton, F.O.B. Plant)

West Kentucky Seam

No. 11 Seam

Sewell Seam

Pocahontas Seam